This document was submitted to EPA by a registrant in connection with EPA's evaluation of this chemical, and it is presented here exactly as submitted.

Dow AgroSciences LLC 9330 Zionsville Road Indianapolis, IN 46268-1054

67/089 4+ 3403

308, 2A October 19, 1999



via Fax: 703-308-8041
Mr. Mark Hartman
Product Manager
Special Review and Reregistration Division
United States Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

Dear Mr. Hartman:

Pursuant to your phone message, Dow AgroSciences would like to clarify issues regarding confidentiality of our responses to the chlorpyrifos preliminary risk assessment documents. As stated in our responses, and again in our letter of October 15 to Ms. Marcia Mulkey, Dow AgroSciences makes no claims of confidentiality to our submission entitled Dow AgroSciences' Response to U.S. EPA's Preliminary Risk Assessment for Chlorpyrifos, Health Effects Division Chapter Dated July 23, 1999, and Dow AgroSciences' Response to U.S. EPA's Draft Reregistration Eligibility Science Chapter for Chlorpyrifos, Fate and Environmental Risk Assessment Chapter Dated November 24, 1998. As such, we request a docket classification of "A" for both of the aforementioned submissions.

Sincerely,

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STUDY TITLE

Dow AgroSciences' Response to U.S. EPA's Draft Reregistration Eligibility Science Chapter for Chlorpyrifos, Fate and Environmental Risk Assessment Chapter Dated November 24, 1998

DATA REQUIREMENT

None

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STUDY COMPLETED ON

15-January-1999

PERFORMING LABORATORY

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LABORATORY STUDY ID

GH-C 4873

STATEMENT OF NO DATA CONFIDENTIALITY CLAIMS

Title:	Dow AgroSciences' Response to U.S. EPA's Draft Reregistration Eligibility
	Science Chapter for Chlorpyrifos, Fate and Environmental Risk Assessment
	Chapter Dated November 24, 1998

Chlorpyrifos

Compound:

No claim of confidentiality is made for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10 (d)(1)(A), (B), or $(C)^*$.

Company:	Dow AgroSciences LLC
Company Agent:	Robert F. Bischoff
1 , 5	
Title:	Regulatory Manager
Signature:	
Date:	

*In the United States, the above statement supersedes all other statements of confidentiality that may occur elsewhere in this report.

THIS DATA MAY BE CONSIDERED CONFIDENTIAL IN COUNTRIES OUTSIDE THE UNITED STATES.

STATEMENT OF COMPLIANCE WITH GOOD LABORATORY PRACTICE STANDARDS

Title: Dow AgroSciences' Response to U.S. EPA's Draft Reregistration Eligibility Science Chapter for Chlorpyrifos, Fate and Environmental Risk Assessment Chapter Dated November 24, 1998

Study Completion Date: 15-January-1999

This study does not meet the definition of a GLP study as it appears in:

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Executive Summary

Dow AgroSciences LLC (Dow AgroSciences) is submitting these comments in response to EPA's Environmental Fate and Effects Division (EFED) preliminary risk assessment for chlorpyrifos (dated November 24, 1998). Because of the limited time available for responding to the Agency and, unfortunately, the tremendous number of errors and omissions found in the Agency's risk assessment, our response should be considered preliminary. Dow AgroSciences intends to submit supplemental comments during the public comment period.

Dow AgroSciences believes the extensive use of chlorpyrifos during the last three decades is a clear indication of the value of this compound and the benefits that chlorpyrifos provides to growers and the American public generally. Dow AgroSciences has developed a comprehensive database to support the continued registration of chlorpyrifos and believes a refined risk assessment utilizing this database demonstrates that realistic risk concerns are minimal and are clearly outweighed by the significant benefits provided by chlorpyrifos.

Dow AgroSciences is the principal registrant and major producer of chlorpyrifos and offers a wide range of end-use products for both agricultural and non-agricultural markets. In addition, Dow AgroSciences sells manufacturing concentrate to third parties for formulation into other registered products. Dow AgroSciences has provided EPA with all studies requested since the first draft chlorpyrifos reregistration standard was promulgated in 1984. Dow AgroSciences has also committed substantial resources to develop stewardship programs for chlorpyrifos products and to conduct voluntary studies in the areas of ecotoxicology, environmental fate, and risk assessment to better understand the effects and fate of this molecule. Virtually all of this activity has been communicated to the Agency by submission of study reports and by face-to-face meetings between representatives of Dow AgroSciences and EPA. Dow AgroSciences is disappointed that EFED did not consider much of this body of work in the preliminary risk assessment. Dow AgroSciences expects EPA to meet its statutory data review obligations in

FIFRA's reregistration procedure provisions, FIFRA §4, in order to make a scientifically justifiable determination as to chlorpyrifos' eligibility for reregistration pursuant to FIFRA §3.

Dow AgroSciences believes that EPA's EFED failed to apply sound scientific principles in conducting the ecological risk assessment and drinking water exposure assessment for chlorpyrifos. Screening-level risk quotient procedures are used in combination with an arbitrary selection of data from laboratory and field studies and incident reports to arrive at unreasonable and indefensible quantitative risk characterizations of chlorpyrifos. In taking this approach, the Agency has ignored recommendations made by its own Scientific Advisory Panel (SAP). The SAP's criticism of the Agency's approach included, but was not limited to, the following:

- The SAP suggested that the Agency's methodologies have a number of limitations, some severe, in relation to their utility in risk assessments.
- The SAP indicated that exposure and effects methodologies used do not provide the depth of understanding of the chemical and biological mechanisms that an environmental risk assessment requires.
- The SAP indicated that the Agency's approach in the extrapolation of laboratory data has not been adequately investigated and validated.
- The SAP indicated that the Risk Quotient is a qualitative parameter and not a highly quantitative measure of ecological risk.
- The SAP suggested that establishing an estimated environmental concentration (EEC) based solely on application rate needed justification.
- The SAP recommended that the Agency should move from deterministic to probabilistic types
 of assessments.

Dow AgroSciences supports the recommendations of the Agency's SAP. Dow AgroSciences believes the procedures currently employed by the Agency fail to yield meaningful results and

¹SAP Comments, meeting of May 29-31, 1996. http://www.epa.gov/oppefed1/ecorisk/sapreprt.htm

recommends all the relevant information available for chlorpyrifos be examined to refine the screening-level assessments to realistically assess environmental risk.

In an attempt to advance the state of the science and characterization of potential environmental risk, Dow AgroSciences commissioned two panels of academic expert scientists to conduct refined aquatic and terrestrial ecological risk assessments. After assembling all existing data on effects and exposure, the panels completed thorough risk assessments, incorporating the sound science recommended by EPA in their Guidelines for Ecological Risk Assessment. The panels concluded that, overall, the potential for ecologically significant risk is low. Dow AgroSciences is committed to following up on the recommendations of the expert panels to better understand site-specific conditions where these ecological concerns may be present. Dow AgroSciences intends to address any realistic concerns and looks forward to working with EPA to develop an appropriate product stewardship program.

This document comments on the following topics covered in the preliminary risk assessment:

- chlorpyrifos use patterns;
- chemical and environmental fate properties of chlorpyrifos and its principal degradate, TCP;
- aquatic and terrestrial exposure profiles, including both modeling and monitoring; and
- aquatic and terrestrial effects profiles, including laboratory toxicity studies, field studies, and incident reports.

Also discussed are examples of corrected risk quotients for key chlorpyrifos uses and refinement of ecological risk assessments beyond the screening level represented by the preliminary risk assessment.

The brief summary comments that follow are discussed in more detail in Section II of this document. All detailed analysis, including data, assumptions, and calculations are provided in

¹ EFED's Summary of the SAP Review of Ecological Risk Assessment Methodologies, April 14, 1997. http://www.epa.gov/oppefed1/ecorisk/efedsum.htm

voluminous appendices that are referenced in Section II. A separate reference section lists all of the citations found throughout this document.

Use Patterns

- Several of EFED's assessments are based on use patterns and use rates which contain significant errors as well as errors in interpretation of labeled use directions.
- Many of the assessments use scenarios that have little, if any, relevancy to typical use of chlorpyrifos in agricultural production systems or in non-agricultural settings.
- Typical use should represent the most commonly applied rate, application method and number
 of applications per season for a given crop system or non-agricultural setting within the
 context of labeled use as implemented by users of the product. This differs significantly from
 the average of use data selected by EFED to represent typical use.
- Modeling of nonexistent formulations (example: agricultural corn cob granule) and construction of exposure scenarios that are physically impossible (example: wildlife drinking from spray-to-runoff applications) are among the most severe errors.

Chemical and Environmental Fate Properties

The Agency fails to fully consider the large body of Dow AgroSciences submissions and
literature data on the environmental fate properties for the primary degradate of chlorpyrifos,
TCP, even though the environmental fate properties of this chemical are used extensively as
inputs in EFED's modeling and risk characterization.

Aquatic Exposure Profile

- The Agency fails to employ their own guidance in choosing appropriate input values for modeling when there are multiple data points available.
- PRZM/EXAMS and GENEEC modeling runs are not documented. Without documentation, it
 is difficult, if not impossible, to make any evaluation of the applicability or quality of the
 Agency's modeling results found in this document.

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 The use of PRZM/GENEEC for simulating the fate of chlorpyrifos in granular formulations is invalid, since neither model adequately accounts for the release characteristics from the granule.

- The assumed aerobic aquatic dissipation for chlorpyrifos in water is non-existent (half-life of infinity). However, uncited field and laboratory studies suggest the true half-life is approximately 7.1 days at the 10% exceedence probability (i.e., 90% of the time, the half-life is less than this value).
- The use of GENEEC or PRZM/EXAMS for estimating estuary concentrations is a blatant misuse of the models, outside of the range in which they have been validated or were intended to be used.
- As acknowledged by the Agency, the standard farm pond scenario is not representative of a
 drinking water source. Therefore, GENEEC or PRZM/EXAMS modeling runs employing
 this scenario are not applicable to drinking water exposure assessment.
- Kinetic modeling clearly demonstrates that TCP is unlikely to be transported in surface runoff
 to surface water sources of drinking water at the high levels predicted by EFED GENEEC
 simulations.
- It is inappropriate to use SCI-GROW for metabolite ground water concentrations unless the molecule is instantaneously converted to 100% of the metabolite upon application. Based on the body of research on the metabolism of chlorpyrifos, this is a virtual impossibility.
- Dow AgroSciences agrees with EFED's statement that TCP is not toxic (not considered to be
 a metabolite of toxicological concern). Therefore, Dow AgroSciences suggests that EFED
 restrict its surface water and groundwater exposure assessments to the parent chlorpyrifos
 molecule, for which there are human health effect levels established for risk assessment.
- Surface water monitoring data more accurately represent exposure of aquatic organisms to
 chlorpyrifos in the flowing water of actual watersheds than do the computer estimated EECs
 for a one-acre farm pond. Dow AgroSciences cites data analysis demonstrating widespread
 chlorpyrifos use in monitored watersheds that are vulnerable to runoff.

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- Dow AgroSciences agrees with EFED's statement in the Water Resource Assessment section
 of the draft science chapter that monitoring for chlorpyrifos in surface water sources of
 drinking water is not necessary.
- Dow AgroSciences disagrees with EFED's assertion that TCP may be a concern in drinking water derived from surface water. EFED fails to fully consider the large body of Dow AgroSciences submissions and literature data on the environmental fate properties of TCP.
- EPA OPP has previously recognized that well and surface water contamination is an industry issue related to the use of all products as liquid, soil-applied termiticides. This recognition led to the issuance of PR Notice 96-7 (EPA 730-N-96-006 dated October 1, 1996), which required all manufacturers of liquid termiticides to adopt common label use directions which would reduce the probability of future water contamination regardless of the termiticide used.
- Chlorpyrifos is one of the most extensively studied pesticides and therefore has a comprehensive data base containing laboratory and field observations. Any assessment, having such a wealth of information available, should utilize this information to its fullest potential to address "real" exposure and the probability of occurrence. This is manifest in a Memorandum from Fred Hansen, U.S. EPA Deputy Administrator concerning the use of probabilistic techniques in Risk Assessment where he stated "The policy explains that such probabilistic analysis techniques as Monte Carlo analysis, given adequate supporting data and credible assumptions, can be viable statistical tools for analyzing variability and uncertainty in risk assessments". Data on chlorpyrifos exists such that probabilistic exposure predictions can and are offered as a refinement to earlier and more simplistic assessment tiers.

Terrestrial Exposure Profile

 The estimates of exposure to wildlife from consumption of plants and invertebrates rely on the Kenaga nomogram method (as modified by Fletcher). A more rigorous examination of field residue data would have allowed the Agency to make a more scientifically-defensible wildlife

¹ USEPA Memorandum, May 15, 1997 from Fred Hansen, Deputy Administrator. Subject: Use of Probabilistic Techniques (Including Monte Carlo Analysis) in Risk Assessment. http://www.epa.gov/ORD/spc/probcovr.htm

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dietary risk assessment. (Corrected risk quotients provided by Dow AgroSciences demonstrate the use of actual chlorpyrifos residue data to estimate exposure.)

- The "Fate Model" used by EFED for estimating plant residue values from multiple
 applications is not available to registrants, nor are the modeling runs documented in the draft
 science chapter.
- Release characteristics of chlorpyrifos granular formulations govern the dose a bird may receive from ingesting granules. This is neglected in EFED's scenario construction.

Aquatic Effects Profile

- EFED did not appropriately deal with issues of data quality and multiple studies of the same organism. The selection of studies used by EFED in support of its aquatic toxicity assessment on chlorpyrifos would appear to be driven only by the lowest-available endpoint concentration, e.g., EC/LC₅₀ value, for a standard test species. For those organisms having more than one study examining the toxicity of chlorpyrifos, EFED's selection of available aquatic toxicity data for chlorpyrifos should be based on a study characterization algorithm such as the Species Mean Acute Value (SMAV) recommended by EPA in support of the Great Lakes Initiative.
- EFED authors overlooked an extensive series of detailed experiments conducted at the
 Winand Staring Centre in the Netherlands that examined the responses of pond ecosystems to
 chlorpyrifos exposure. A brief summary of these important experiments is presented.
- EFED cites single-species toxicity testing of ambient surface water samples in California as
 evidence of adverse ecological effects. Dow AgroSciences presents information on the
 limitation of such testing to predict in-stream ecological impact.
- EFED did not discuss the low magnitude and infrequent nature of the chlorpyrifos fish tissue residues in the EPA National Fish Survey, thus misrepresenting the significance of these results.
- There is no evidence, scientific or otherwise, that the use of chlorpyrifos is responsible for the global decline in amphibian populations. This trend is observed world-wide, including areas where chlorpyrifos usage is minimal or non-existent.

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 Because there are no references for any of the freshwater incident reports summarized by EFED, it is difficult for Dow AgroSciences to determine whether the database reviewed by EPA duplicates our information.

After more than three decades of chlorpyrifos use and numerous applications, relatively few
aquatic incidents have occurred. A comprehensive, weight-of-the-evidence analysis that
considers laboratory data, fate data, and incident information clearly demonstrates that
chlorpyrifos does not cause the frequent fish kills predicted by EFED's screening-level
assessments.

Terrestrial Effects Profile

- Dow AgroSciences disagrees with EFED's use of a single, quality insensitive, data selection criterion such as "lowest toxicity value" without due regard to the integrity and quantity of the data. If there is more than one toxicity value for a given species and there is reasonable assurance of data quality for each value, the geometric mean of these values represents a conservative estimate of the "true" sensitivity of the species and should be used when conducting risk assessments.
- EFED acknowledges that granular chlorpyrifos products are less toxic (i.e., less hazardous)
 than technical grade chlorpyrifos. Dow AgroSciences therefore suggests that the toxicity
 profile for granules be based on empirical data on granular formulations for both rodent and
 avian species.
- EFED used lowest mammalian acute oral LD₅₀ values to calculate estimated 1-day LC₅₀ values. This procedure should only be used when no LC₅₀ values are available and then with reservation and restrictions. Dow AgroSciences provides a more scientifically sound approach based on EPA recommendations to calculate 1-day LC₅₀ values.
- EFED has chosen to utilize toxicity data in their assessment of chlorpyrifos that normally
 would not meet their own established standards. In many cases the data are cited from
 secondary and tertiary sources, are unvalidated, and yet are used by EFED as the driver values
 for the risk assessment.

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 EFED has also failed to utilize some Dow AgroSciences reports and published data in their toxicity and exposure assessments.

- Interpretation of a large pen, simulated field study is severely flawed.
- There are numerous errors with regard to EFED's review of the three terrestrial field studies.
 Examples discussed in detail include misrepresentation of casualty classifications, incorrect data tables, and errors in interpreting search intensity and chemical analysis of carcasses.

Corrected Risk Quotients

- Dow AgroSciences has discovered numerous errors in the risk quotients presented in the EFED draft science chapter and intends to provide corrections for all erroneous values during the 60-day public comment period.
- For this 30-day response document, Dow AgroSciences will restrict its comments to correcting risk quotients for three example use patterns that represent major typical agricultural and non-agricultural uses of chlorpyrifos.
- Corrections were made for numbers of applications and use rates, terrestrial and aquatic
 toxicity, and terrestrial and aquatic exposure. In cases where the methods used by EFED
 were determined to be inappropriate, more scientifically defensible methods were substituted
 to make the corrections.
- In general, the corrected risk quotients are substantially lower than the overly conservative risk quotients calculated by EFED. However, for some organisms, particularly some aquatic species, certain risk quotients still exceed levels of concern. Dow AgroSciences proceeded to refine the terrestrial and aquatic risk assessments to obtain more realistic, higher tier, risk characterizations. When this was done most concerns disappeared. The few remaining concerns will be addressed by Dow AgroSciences' product stewardship programs.

Refinement of Ecological Risk Assessments

All of the ecological risk assessments presented in the draft EFED science chapter were
conducted at a screening level, with weight-of-evidence analysis restricted only to those few
studies and incident reports selectively chosen to support the conclusion of LOC exceedences.

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• EFED inappropriately utilizes the Tier I and II risk assessments and incomplete weight-ofevidence evaluation to characterize risk from chlorpyrifos use and to compare the relative risk of chlorpyrifos use to risk associated with use of other insecticide products.

- This inappropriate use of screening methods runs counter to the recommendations of the Aquatic Risk and Mitigation Dialogue Group.
- The U.S. EPA FIFRA SAP also has serious concerns over the lack of probabilistic assessment approaches and the reliance on the use of risk quotients in EFED's ecological risk assessment activities.
- Use of single-point risk quotients in the EFED document presumes that these simple values characterize or quantitate risk to organisms in complex natural ecosystems, an assumption which has failed to be proven for the risk quotient values calculated for chlorpyrifos.
- Dow AgroSciences therefore advocates refinement of the chlorpyrifos ecological risk
 assessments wherever correctly calculated risk quotients exceed EFED's screening levels of
 concern. Dow AgroSciences is disappointed that EFED did not progress beyond the
 screening level of assessment, once levels of concern were identified for chlorpyrifos. Dow
 AgroSciences has completed higher tier assessments and has submitted them to EPA.
- As a general approach to risk assessment for chlorpyrifos, Dow AgroSciences advocates the
 principles described in the 1992 EPA ecological risk assessment framework, the 1996
 proposed guidelines, and the 1998 final guidelines. The principles set forth in these EPA
 guidance documents are endorsed by the Society of Environmental Toxicology and Chemistry
 and Cal/EPA.
- In order to obtain refined, unbiased assessments based on sound science, Dow AgroSciences
 assembled two expert panels of independent academic scientists and consultants to conduct
 the best aquatic and terrestrial ecological risk assessments possible with existing data. Both
 assessments followed the EPA guidance on ecological risk assessment. They were submitted
 to EPA in December, 1998.
- Overall, the aquatic expert panel concluded that existing data do not suggest ecologically significant risks, except in a few locations. Dow AgroSciences is committed to conducting

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site-specific risk assessments and applying appropriate product stewardship to these locations where risk may exist.

- The terrestrial panel concluded that the use of chlorpyrifos in corn agroecosystems will not
 result in widespread and repeated mortality of terrestrial wildlife, particularly birds and
 mammals. Widespread and repeated mortality is the EPA's stated standard for assessing
 potential for pesticide effects on avian species.
- Dow AgroSciences expects EFED to review the expert panel ecological risk assessments and subsequent similar assessments and utilize the findings to refine the screening level assessments presented in the draft science chapter. Dow AgroSciences believes that refined risk assessments will demonstrate that most (or essentially all) uses of chlorpyrifos present no unreasonable (or undue) risk concern. In those few cases in which a refined risk assessment identifies realistic risk concerns, Dow AgroSciences is prepared to work with the Agency to implement product stewardship measures to address those concerns.

I. Introduction

This document corrects errors in EFED's ecological risk assessments and drinking water exposure assessment, identifies uncited studies previously submitted by Dow AgroSciences, lists omissions of other relevant data, and presents differences in interpretation of evidence. Additionally, Dow AgroSciences stresses the important distinction between screening methods of assessment, designed to identify pesticide products that do not pose any risks to non-target organisms or humans, and true quantitative risk assessments that characterize the probability of occurrence of an adverse effect. EFED has presented in this draft science chapter only screening levels of assessment which cannot predict actual risk from the use of chlorpyrifos. The general structure and tone of the draft science chapter suggests that EFED started with the premise that chlorpyrifos poses significant risks to non-target organisms and humans and then selectively assembled evidence to support this view. This is an example of unsound science that is completely unacceptable for regulatory decision making. Dow AgroSciences has recently submitted refined ecological risk assessments following EPA guidelines that we expect EFED to review and use to improve their risk characterization of chlorpyrifos.

The remainder of this document presents specific comments on the following topics covered in the draft science chapter: chlorpyrifos use patterns; chemical and environmental fate properties of chlorpyrifos and its principal degradate, TCP; aquatic and terrestrial exposure profiles, including both modeling and monitoring; and aquatic and terrestrial effects profiles, including laboratory toxicity studies, field studies, and incident reports. Also discussed are examples of corrected risk quotients for key chlorpyrifos uses and refinement of ecological risk assessments beyond the screening level represented by the draft science chapter. Section II presents the key points of our commentary.

Dow AgroSciences intended to summarize the errors found in the draft science chapter to assist EFED authors in error correction, as requested in EPA's cover letter on the document. Due to the large numbers of errors found, however, this proved not to be feasible. Instead, the individual errors are collected into a series of appendices that conform to the topical structure of

commentary outlined in the preceding paragraph. Each subsection of Section II refers the reader to the appropriate appendix listing the detailed errors, corrections, references to uncited studies and other relevant data, and differences in interpretation.

II. Comments on Errors, Uncited Studies, Omissions of Other Relevant Data, and Differences in Interpretation of Evidence

A. Chlorpyrifos Use Patterns

1. Agricultural Uses

EPA identifies several uses and use rates that seem to be driving the risk assessments. Several of these assessments are based on use patterns and use rates containing significant errors as well as errors in interpretation of labeled use directions. In addition, many of the assessments use scenarios that have little, if any, relevancy to typical use of chlorpyrifos in agricultural production systems.

Throughout the document, EFED references BEAD quantitative use information for chlorpyrifos to develop scenarios of "typical use" on several crops. Dow AgroSciences agrees with the approach of conducting risk assessments for both typical and worst case scenarios developed from use information, although EFED's approach to identifying "typical use" is flawed. EFED has constructed "typical use" on a given crop from average application rates and average number of applications per year presented in BEAD usage information. Typical use should represent the most commonly applied rate, application method and number of applications per season for a given crop system within the context of labeled use as implemented by users of the product. This differs significantly from the average of use data selected by EFED to represent typical use. (Appendix A.1)

2. Non-Agricultural Uses

EPA identifies termiticide/perimeter and turf and ornamental uses and use rates as key risk assessment drivers. Several of these assessments are based on use patterns and use rates which

contain significant calculation errors as well as errors in interpretation of labeled use directions. In addition, many of the assessments use scenarios constructed that have little, if any, relevancy to typical use of chlorpyrifos in non-agricultural settings. Key examples would be the improper linkage of the termiticide and perimeter treatment applications, followed by the calculation of RQs based on the *assumption* that wildlife could *possibly ingest chlorpyrifos which could have puddled* as a result of the perimeter or ornamental use concentrations and application rates. In fact, the ornamental use labels direct application of chlorpyrifos finished spray to the point that the spray deposition just begins dripping from the leaves; therefore, the probability that wildlife would actually ingest product which had puddled on the surface of the ground is inappropriate. Additionally, the probability of wildlife coming into contact with transient puddling before the solution is absorbed by the ground is relatively remote.

Throughout the document, EFED references BEAD quantitative use information for chlorpyrifos to develop scenarios of "typical use" in the non-agricultural segment. Dow AgroSciences agrees with the approach of conducting risk assessments for both typical and worst case scenarios although EFED's approach to identifying "typical use" is flawed. EFED has constructed "typical use" on a given use pattern from average application rates and average number of applications per year presented in BEAD usage information. Typical use should represent the most commonly applied rate, application method and number of applications per season for a given application type within the context of labeled use as implemented by users of the product. This differs significantly from the average of use data selected by EFED to represent typical use. It is particularly troubling to comment on the EFED chapter with the presence of gross calculation errors, unrealistic use pattern depiction, modeling of nonexistent formulations and inadequate documentation to reconstruct their use pattern calculations. (Appendix A.2)

B. Chemical and Environmental Fate Properties

The Agency fails to fully consider the extensive body of work on fate of both chlorpyrifos and TCP that appears in the open literature, as well as additional Dow AgroSciences submissions.

The most glaring omission is the lack of information on the primary degradate, TCP, even though

the environmental fate properties of this chemical are extensively used as inputs in EFED's modeling and risk characterization analyses. (Appendix B)

C. Aquatic Exposure Profile

1. Modeling

a. <u>Exposure to Non-Target Organisms</u>

The Agency fails to employ their own guidance in choosing appropriate input values for modeling when there are multiple data points available. This guidance has been dutifully employed by registrants in their submissions of modeling studies.

PRZM/EXAMS modeling runs are not documented. The description of the modeling runs, supposedly in Appendix IV of the EFED document, consists only of a summary table. The lack of documentation is in direct conflict with the Agency's own guidance on the performance and documentation of modeling studies as communicated by EFED personnel to the ACPA FIFRA Modeling Working Group in 1995. Registrants, including Dow AgroSciences, have made a good faith effort to follow this guidance in their submission of modeling studies. Without documentation, it is difficult, if not impossible, to make any evaluation of the applicability or quality of the Agency's modeling results found in this document.

The use of PRZM/GENEEC for simulating the fate of chlorpyrifos in granular formulations is invalid, since neither model adequately accounts for the release characteristics from the granule.

The assumed aerobic aquatic dissipation for chlorpyrifos in water is non-existent (half-life of infinity). However, uncited field and laboratory studies suggest the true half-life is approximately 7.1 days at the 10% exceedence probability (i.e., 90% of the time, the half-life is less than this value). Changes in the aerobic aquatic dissipation half-life dramatically alter sub-chronic and chronic modeled exposure predictions and resulting risk quotients (Appendix B).

The use of GENEEC or PRZM/EXAMS for estimating estuary concentrations is a blatant misuse of the model over the range in which it is valid, and any extrapolations to estuary scenarios are unreliable. It is anticipated that most estuaries will have spatially averaged exposure values far below monitored values found in streams and rivers due to the active tidal mixing between the estuary and open water and dilution effects of the estuary itself.

Higher tiered probabilistic/mechanistic exposure assessments, refinements, and/or methodologies have been reviewed and accepted in a variety of peer reviewed scientific journals [Giesy et al. (accepted); Havens et al., 1998; Cryer et al., 1998a; Cryer and Laskowski, 1998; Cryer et al., 1998b; Cryer and Havens (accepted)]. Dow AgroSciences has provided EPA with several of these refined aquatic Tier III probabilistic exposure/risk assessments [Havens et al. (1994); Havens and Peacock (1995); Havens 1995)] for a variety of markets where chlorpyrifos is sold. They were omitted from the EFED draft science chapter. (Appendices C2, B)

b. <u>Exposure to Humans in Drinking Water</u>

(1) Surface Water

The use of GENEEC or PRZM/EXAMS in the standard farm pond scenario does not represent a source of drinking water. Therefore, results from modeling runs employing this scenario are not applicable to drinking water exposure assessment. Further, EFED appears to assume, incorrectly, a long dissipation half-life for the parent chlorpyrifos molecule but 100% instantaneous conversion to the principal metabolite, TCP. The parent/daughter kinetic transformation routines in PRZM should have been utilized in this simulation to correctly account for the rise and decline of TCP. EFED did not follow their own guidance and document the modeling runs in the draft science chapter. It is therefore difficult for Dow AgroSciences to provide any additional comments on the modeling procedures used.

The kinetic modeling detailed in Appendix C.1 clearly demonstrates that TCP is unlikely to be transported in surface runoff to surface water sources of drinking water at the high levels predicted by the EFED GENEEC simulations.

There is no HAL established for TCP, nor is TCP included in the tolerance expression for chlorpyrifos. It is not considered to be a metabolite of toxicological concern. Dow AgroSciences therefore suggests that EFED restrict its surface water exposure assessment to the parent chlorpyrifos molecule, for which there are human health effect levels established for risk assessment.

(2) *Groundwater*

Groundwater concentrations for the major metabolite of chlorpyrifos (TCP) are predicted using SCI-GROW, an empirical model based upon prospective groundwater study observations. It is inappropriate to use SCI-GROW for metabolite ground water concentrations unless the parent material is instantaneously converted to 100% of the metabolite upon application. This is a poor assumption for agricultural applications of chlorpyrifos and virtually impossible for persistent termiticidal barrier treatments. Unfortunately, the EFED SCI-GROW modeling assumed instantaneous conversion, resulting in unrealistically conservative predictions.

SCI-GROW is not applicable to termiticide barrier treatments, which are protected from rainfall by roof overhang and drainage away from building foundations. The driving force for leaching of chlorpyrifos or TCP from barrier treatments is far less than that associated with the agronomic prospective groundwater studies upon which SCI-GROW is based.

There is no HAL established for TCP, nor is TCP included in the tolerance expression for chlorpyrifos. It is not considered to be a metabolite of toxicological concern. Dow AgroSciences therefore suggests that EFED restrict its groundwater exposure assessment to the parent chlorpyrifos molecule, for which there are human health effect levels established for risk assessment. (Appendix C.1)

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2. Monitoring

a. <u>Exposure to Non-Target Organisms</u>

DowAgroSciences generally agrees with the EFED statement on page 28 of the draft science chapter:

"The monitoring data represent flowing water receiving pesticide loadings from partially cropped, partially treated watersheds much of which is not adjacent to the water body. Therefore, such data may more accurately represent exposure of aquatic organisms to chlorpyrifos in the flowing water of actual watersheds than the computer estimated EECs for a one-acre farm pond."

However, analysis of all available information for the periods in which much of the monitoring was conducted (Giesy et al., 1998; Giesy et al., in press) indicates that the statement, "such data may more accurately represent exposure", should actually read "such data do more accurately represent exposure."

Dow AgroSciences disagrees with this statement from the same page:

"Although there is substantial overlap between a number of USGS stations and chlorpyrifos use sites, sampling sites do not necessarily represent watersheds where chlorpyrifos is most heavily used. Therefore they may reflect less exposure to chlorpyrifos than in watersheds where it is heavily used."

Dow AgroSciences' unpublished report GH-C 4660, submitted November 18, 1998 (Giesy et al., 1998) (also Giesy et al., in press) presents data demonstrating widespread chlorpyrifos use in monitored watersheds that are vulnerable to runoff.

EFED omits a key surface water monitoring publication (Richards and Baker, 1993). This study reports multiple-year data from time-stratified, event-driven sampling that effectively captures both peak and long-term average pesticide concentrations in Midwestern agricultural watersheds vulnerable to runoff. It is generally recognized in the scientific community as the most

comprehensive monitoring study conducted to date. Further, significant amounts of chlorpyrifos are used in these watersheds. The Richards and Baker publication was summarized in DowElanco submission MRID 43823901 (Poletika, 1995), which is not cited in the draft science chapter. The study is on-going, and more recent data are also available.

b. Exposure to Humans in Drinking Water

(1) Surface Water

Dow AgroSciences agrees with EFED's statement in the Water Resource Assessment section of the draft science chapter on page 22 that monitoring for chlorpyrifos in surface water sources of drinking water is not necessary. EFED later contradicts itself by suggesting that existing data are inadequate (see Appendix C.2 for Dow AgroSciences responses to this contradictory analysis). Dow AgroSciences disagrees with the EFED assertion on page 22 that TCP may be a concern in drinking water derived from surface water. Evidence this assertion is incorrect includes the environmental fate properties of TCP in surface terrestrial/water systems (largely ignored by EFED) that limit TCP transport and persistence and the classification of TCP as a metabolite of no toxicological concern. (Appendices B, C.1, C.2)

(2) Groundwater

The characterization of contaminated drinking water wells in the draft science chapter is erroneous for several reasons. All of the incidents are associated with termiticide barrier treatments, but well contamination from this type of chlorpyrifos use is not chemical specific. In fact, EPA OPP has previously recognized that this is an industry issue related to the use of all products as liquid, soil-applied termiticides. This recognition led to the issuance of PR Notice 96-7 (EPA 730-N-96-006 – dated October 1, 1996), which required all manufacturers of liquid termiticides to adopt common label use directions which would reduce the probability of future water contamination regardless of the termiticide used.

Well contamination occurs at the time of application by preferential saturated flow to the well bore hole, and after the emulsion dries the chlorpyrifos is immobilized by sorption to soil particles.

This greatly reduces the probability of any significant further transport. It is the well that is contaminated, not the aquifer, so well remediation is a practical mitigation. Although the frequency of well contamination is very low (Thomas and Chambers, 1997), Dow AgroSciences recognizes there is the potential for adverse human health effects in a very small sub-population of the U.S. and has voluntarily implemented a product stewardship program that minimizes exposure of affected residents to chlorpyrifos residues in drinking water wells. Therefore, there is no exposure level or duration that is significant relative to any meaningful toxicity threshold value, and the well is restored to its previous condition.

EFED misinterprets the well monitoring for TCP in the citrus field study (MRID 40059001) and states that only a 50 μ g/L detection is reportable. Examination of the data tables in the submitted report indicates that gross residues down to 2 μ g/L were found and reported. Moreover, the average TCP concentration was considerably lower than 50 μ g/L. The EFED assertion that vulnerable groundwater used for drinking water may be contaminated with TCP at a level of up to 50 μ g/L is not supported by these data.

The maximum value for chlorpyrifos detection in the Pesticides in Ground Water Database of $0.65 \,\mu g/L$ cited by EFED does not agree with the maximum reported by NAWQA and may well represent point source contamination. The maximum value should be interpreted in relation to the entire distribution of concentrations. (Appendix C.2)

D. Terrestrial Exposure Profile

1. Modeling

The "Fate Model" used by EFED for estimating plant residue values from multiple applications is not available to registrants, nor are the modeling runs documented in the draft science chapter. The description of the modeling runs, supposedly in Appendix III of the document, consists only of a title page. The lack of documentation and unavailability of the model are both in direct conflict with the Agency's own guidance on the performance and documentation of modeling

studies as communicated by EFED personnel to the ACPA FIFRA Modeling Working Group in 1995. Registrants, including Dow AgroSciences, have made a good faith effort to follow this guidance in their submission of modeling studies. Without documentation, it is difficult, if not impossible, to make any evaluation of the applicability or quality of the Agency's modeling results found in this document.

Release characteristics of chlorpyrifos granular formulations govern the dose a bird may receive from ingesting granules. A methodology to describe chlorpyrifos release from clay granules is given elsewhere (Cryer and Laskowski, 1994, 1998). The predicted median release interval for all the chlorpyrifos mass within the clay granule formulation to be removed ranged from 11 - 17 days for Midwestern corn (Cryer and Laskowski, 1994), illustrating the relatively short time window for avian and mammalian exposure due to ingestion. (Appendix C.1)

2. Monitoring

The estimates of exposure to wildlife from consumption of plants and invertebrates rely on the Kenaga nomogram method (as modified by Fletcher). EPA scientists have written about the uncertainty and potential error which can result (Pfleeger et al., 1996) and recommend the use of measured residue values when available. An extensive set of field residue data is readily accessible for chlorpyrifos in Dow AgroSciences submissions; however, this data source was referred to in only a selective fashion in the Agency's attempt to justify their use of the Kenaga/Fletcher method. A more rigorous examination of this data would have allowed the Agency to make a more scientifically-defendable wildlife dietary risk assessment. (Appendix D)

E. Aquatic Effects Profile

1. Laboratory Toxicity Studies

The selection of studies used by EFED in support of its aquatic toxicity assessment on chlorpyrifos would appear to be driven only by the lowest-available endpoint concentration, e.g., EC/LC₅₀ value, for a standard test species. For those organisms having more than one study examining the toxicity of chlorpyrifos, EFED selection of available aquatic toxicity data for

chlorpyrifos should be based on a study characterization algorithm, such as that utilized by the U.S. EPA guidance document for the Great Lakes Initiative (U.S. EPA, 1995).

The EFED authors clearly did not choose to enforce a standard study selection algorithm prioritized on flow-through exposures and measured dose concentrations, as studies appeared to have been selected for EFED simply by the lowest effect concentration for a given toxic impact to a standard test species. If we instead use all available toxicity data for a given species and employ standard exposure durations, it is possible to generate "revised" acute and chronic toxicity effect concentrations to replace those used by EFED in their calculation of aquatic RQ values on chlorpyrifos. These revised concentrations are presented for standard freshwater and saltwater organisms. The revised effect concentrations were selected from the mean toxicity concentration (SMAV or NOEC) for standard freshwater and saltwater organisms with a exposure duration of either 48 or 96 hours for invertebrate or vertebrate test species, respectively. (Appendix E.1)

2. Field Studies/Biomonitoring

In the EFED review of freshwater microcosm/mesocosm/field studies on chlorpyrifos (pp 73-83), the reviewers have excluded a substantial amount of information on the fate and effects of the compound in these complex aquatic systems. The EFED authors overlooked an extensive series of detailed experiments conducted at the Winand Staring Centre in the Netherlands that examined the responses of pond ecosystems to chlorpyrifos exposure. A brief summary of these important experiments is presented. Information based on microcosm/mesocosm data are of considerable value to an in-depth risk assessment since these systems are better able to replicate the interactions in dynamic ecological communities.

The EFED document fails to cite the published research of Kuivila and Foe (1995), who determined that chlorpyrifos did not play a major or controlling role in bioassay mortality observed in their January-February 1993 water samples from San Francisco, CA. These results were contrary to the conclusions noted in the EFED document (p 32). The single citation noted

in this portion of the EFED document, Foe (1995), could not be found in the EFED reference listing.

EFED anecdotally cites single-species toxicity test results from ambient surface water samples as evidence of adverse ecological effects. Given the demonstrated tendency for *Ceriodaphnia* tests to indicate toxicity in the absence of observable ecological effects in the field, the results of such bioassay toxicity tests should <u>not</u> be used as the only reliable evidence of instream biological impact. Bioassays were originally designed as "screening methods" to identify potentially toxic conditions, not as final quantitative indicators of ecological impacts.

The EFED document notes (p 33) that fish residue data on chlorpyrifos have been collected in a nationwide monitoring study (U.S. EPA, 1992). When examined as a cumulative frequency distribution on all 362 U.S. sites where fish were collected, the 90th and 75th percentile chlorpyrifos fish residue concentrations were approximately 11 and 0.8 µg/kg (ppb), respectively, and ~75% of fish concentrations at all sites were below the analytical detection limit (0.05 µg/kg). However, the EFED authors did not discuss the low magnitude and infrequent nature of the chlorpyrifos residues; it was merely noted that these data demonstrate "extensive off-field movement and exposure of chlorpyrifos to aquatic organisms."

It was also disconcerting that EFED is willing to utilize field observations when adverse effects are observed, but failed to use field information in refining their model predictions, i.e., the levels of chlorpyrifos residues in fish. Using the EFED model for chlorpyrifos residues in fish, the fish concentrations should vary from ~2 - 40 ppm in whole fish or from 3 - 57 ppm in viscera. A comparison of these estimates to the EPA-measured whole fish residues for chlorpyrifos at 362 U.S. sites reveals that the estimated fish residues exceeded the 90th percentile field concentration for chlorpyrifos (11 ppb) by 180-3600 times. (Appendix E.2)

3. Incident Reports

There is no evidence, scientific or otherwise, that the use of chlorpyrifos is responsible for the global decline in amphibian populations. This trend is observed even in areas where chlorpyrifos usage is minimal or non-existent.

Dow AgroSciences has analyzed all known surface water contamination incidents involving fish kills that resulted from legal use of products containing chlorpyrifos. Because there are no references for any of the freshwater incident reports summarized by EFED, it is difficult for Dow AgroSciences to determine whether the data base reviewed by EPA duplicates our information.

As EFED recognizes in the draft science chapter, most of these relatively few incidents are related to termiticide applications. The draft EFED science chapter makes reference to reported detection of chlorpyrifos in surface water following a termiticide application. These references fail to recognize surface water detection of chlorpyrifos has previously been identified by the EPA OPP as an industry issue related to the use of all products as liquid, soil-applied termiticides. This recognition led to the issuance of PR Notice 96-7 (EPA 730-N-96-006 – dated October 1, 1996), requiring all manufacturers of liquid termiticides to adopt common label use directions which would reduce even further the low probability of water contamination regardless of the termiticide used.

The definition of an insecticide is a chemical that kills insects. Dow AgroSciences is not familiar with any insecticide that does not adversely affect any non-target organisms. Chlorpyrifos is highly toxic to many aquatic organisms. Therefore, it is not surprising that there are some reports of aquatic incidents. It should be noted, however, that after more than three decades of chlorpyrifos use and numerous applications, relatively few aquatic incidents have occurred. In a weight-of-the-evidence, risk/benefit analysis, chlorpyrifos clearly does not cause the widespread and repeated mortality predicted by EFED screening level assessments. (Appendix E.3)

4. Aquatic Effects in Terrestrial Field Studies

Three terrestrial field studies (corn, citrus, and turf) were voluntarily submitted to the agency to evaluate the hazard of various formulations of chlorpyrifos to terrestrial animals. During the course of these studies, incidental fish casualties were identified during the citrus and turf studies, but not the corn study. EFED states no information was provided by Dow AgroSciences regarding these incidents (see pp 28, 42, 57, 60, and 198 of the EFED science chapter). This statement is incorrect for the citrus study and misleading for the turf study. A 6(a)(2) report was submitted to the EPA (OPP) on 15 July 1992 and information from the analyses of fish, water, and sediments was provided for the citrus study. The fish kills were due to direct application of chlorpyrifos into ponds adjacent to the citrus because the Lorsban* 4E insecticide label was not properly followed. During the turf study, only 2 of 192 water samples taken from hazards on the treated sites had detectable levels of chlorpyrifos, there was a large number and quantity of additional pesticides used intermittently during the study, and there was an unusual amount of inclement weather. Therefore, it is unlikely that chlorpyrifos was responsible for the fish kills associated with the turf study. (Appendix E.4)

F. Terrestrial Effects Profile

1. Laboratory Toxicity Studies

Dow AgroSciences disagrees with EFED's use of a single, quality insensitive, data selection criterion such as "lowest toxicity value" without due regard to the integrity of the data. This subjective approach is inconsistent with the Agency's stated position that each report "should include all information necessary to provide a complete and accurate description of test procedures and evaluation of the test results" (U.S.EPA, 1982). Furthermore Standard Evaluation Procedures (SEP) have been developed by the EPA to ensure "...comprehensive and consistent treatment of the science in reviews..." of data used in risk assessments (Urban and Cook, 1986). Ideally, if there is more than one toxicity value for a given species and there is

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reasonable assurance of data quality for each value, the geometric mean of these values represents a conservative estimate of the "true" sensitivity of the species and should be used when conducting risk assessments (U.S.EPA, 1995).

On page 19 EFED presents a table to illustrate the number of granules/LD₅₀. However, EFED chose to use toxicity values for **technical chlorpyrifos** rather than use values for the formulated granules. EFED acknowledges (p 41) that "...granular chlorpyrifos products...are less toxic (i.e., less hazardous) than technical grade chlorpyrifos." Dow AgroSciences therefore suggests that the table on page 19 represent toxicity to granules based on empirical data on granular formulations for both the rodent and avian species. A revised table is provided in Appendix F.

EFED used lowest mammalian acute oral LD_{50} value to calculate estimated 1-day LC_{50} values. This procedure should only be used when no LC_{50} values are available and then with "reservation and restrictions" (Urban and Cook, 1986). Dow AgroSciences provides a more scientifically sound approach, based on the recommendations of the EPA (Urban and Cook, 1986), to calculate 1-day LC_{50} values (see Appendix F).

Dow AgroSciences believes only studies that follow the EPA's stringent guideline criteria established for data submission and have undergone a quality review should be used for a Tier I risk assessment such as presented in the EFED document. Unfortunately, EFED has chosen to utilize toxicity data in their assessment of chlorpyrifos that normally would not meet their own established standards. For example, on pages 41-47 EFED provides a summary of acute oral and acute dietary toxicity data on different species of birds. In many cases the data are cited from secondary and tertiary sources. Use of such data raises a high level of concern within Dow AgroSciences as to the appropriateness of the data for use in a risk assessment of this magnitude. For these studies it is apparent that EFED did not have the original data for statistical analysis to "validate the conclusions" nor assess the experimental design. In may cases invalidated data are used by EFED as the driver values for the risk assessment. Not surprisingly, most of these values are the lowest values reported. Dow AgroSciences strongly objects to EFED's use of a single,

quality insensitive, criterion such as "lowest toxicity value" without due regard to the integrity of the data. This subjective approach is inconsistent with stated Agency's stated position that each report "should include all information necessary to provide a complete and accurate description of test procedures and evaluation of the test results" (U.S. EPA, 1982). Furthermore, SEPs have been developed by the EPA to ensure "...comprehensive and consistent treatment of the science in reviews..." of data used in risk assessments (Urban and Cook, 1986).

Below are some of the more egregious examples of EFED's subjective use of data.

- 1. The acute LD₅₀ value for the ring-necked pheasant is cited from Hudson et al. (1984) (MRID 00160000). Hudson et al., 1984 is a compilation of data generated "over a number of years" at the Denver Wildlife Research Center. Much of the information in this document had been published earlier by a number of authors. The data for the pheasant was first published by Tucker and Haegele (1971). These studies were conducted with three to seven birds at each dose group. It is unclear how many pheasants were tested with chlorpyrifos or the nature of the dose response. Despite these failings this study was judged "core" by EFED!
- 2. A clear example of EFED's disregard for data quality analysis and its selective use of data is apparent in its assessment of the acute oral toxicity data for the house sparrow. On page 43 EFED cites three studies on the toxicity of chlorpyrifos house sparrows: Schafer and Brunton (1979, MRID 4037840); Hudson et al. (1984, MRID 00160000); and, Gallagher, et al. (1996, MRID 44057102). EFED elected to use the data of Schafer and Brunton (1979), an LD₅₀ of 10 mg/kg, as the value to be used in their risk assessment. The methods followed during the conduct of this study included the ASTM Recommended Practice for Determining Acute Oral LD₅₀ for Testing Vertebrate Control Agents (E555-75) and methods described by Schafer et al. (1973). The ASTM methodology is quite brief and provides no guidance on the appropriate number of test animals; however, Schafer et al.'s (1973) methodology indicates that two birds were used at each test level, which is far fewer subjects than required by EPA guidelines or for acceptable statistical analysis.

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The source of the sparrow data in Hudson et al. (1984) is Tucker and Haegele (1971). The original authors indicated that for the chemicals tested, three to seven birds were used at each treatment level; it is unclear how many birds were used in their test with Dursban* insecticides. This uncertainty raises serious doubt as to the applicability of the data. Clearly, EFED did not review the raw data for this study to validate the results.

The study by Gallagher et al. (1996) was conducted under GLP and followed stringent EPA guidelines. The validity of this study has been verified by EFED. Inexplicably, EFED chose the data from Schafer and Brunton (1979) to be used in their evaluation of the risk of chlorpyrifos to birds. Dow AgroSciences considers the use of Schafer and Brunton's (1979) data and the exclusion of recent scientifically sound data (Gallagher et al., 1996) in its risk assessment to lack scientific or regulatory justification.

3. One additional example of use of data that lacks scientific validation involves the mammalian acute oral toxicity of chlorpyrifos. Under Mammalian Acute Oral Toxicity Findings (pp 50-51), EFED includes a report on rat toxicity cited from Smith, 1987 (MRID41043901). This "finding" is from a tertiary source. Smith (1987) cites the 1982 version of the "Farm Chemicals Handbook" (Berg, 1982), which is, at best, a secondary source of information itself, as the source of these data. Clearly, these data could not possibly have undergone a quality check to validate the findings. Regardless, EFED uses the reported LD₅₀ value of 97 mg/kg in its assessment of risk simply because it is lowest reported value. There is no credible regulatory, let alone scientific, justification for EFED to use unverifiable data from a tertiary source in its risk assessment while ignoring studies that have undergone regulatory review. Dow AgroSciences strongly objects to EFED's subjective use of such data.

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EFED has also failed to utilize some Dow AgroSciences reports and published data in their toxicity assessment. Dow AgroSciences provides this information as well as comments on errors and omissions. (Appendix F)

2. Field Studies

There are numerous errors with regard to EFED's review of the three terrestrial field studies. Examples of some of the most prominent errors are given below.

Page 54: A large pen, simulated field study is included under Terrestrial Field Studies. This should be considered a worst-case scenario when comparisons are made to field studies. The only statistically significant effect in the study was abnormal behavior in the 6 lb a.i./A treatment. Therefore, NOEL and LOEL are based on abnormal behavior and not mortality. The discussion of omitting mortality that occurred during the last five days of the study is speculative and not good science. There is no discussion about the myriad of parameters measured that were not significantly different for either treatment (3 + 3 or 6 lb a.i./A) compared to the control. EFED concedes that the mean measured, initial chlorpyrifos residues values are well below EFED's predicted EECs. However, no mention is made of the rapid decline in chlorpyrifos residues during this study. (For details, see Appendix F.2.)

Pages 55: Death was not considered treatment-related just because analytical analyses tested positive for chlorpyrifos. This is a misrepresentation of the casualty classification scheme presented in all three studies.

Pages 55, 56-57, and 59-60: The tables on these pages contain a number of errors and do not contain all pertinent data.

Page 56: (1) The distinction between casualty and carcass is dropped. Carcass or casualty may be used for dead animals, but casualty should be used when both dead and abnormally behaving animals are discussed. (2) There are two problems with the following sentence: "Only seven

carcasses (9.6%) were analyzed for chlorpyrifos." First, stating that "Only seven carcasses were analyzed" insinuates that more carcasses could have been analyzed but were not. Second, 16 of 73 (21.9%) total post-treatment casualties or 8 of 44 (18.2%) post-treatment casualties on treated sites were analyzed. (3) "Consequently, out of ten animals for which possible chlorpyrifos effects were actually determined 40% were negative and 60% were positive for chlorpyrifos residues or cholinesterase inhibition." This percentage is incorrectly calculated. Adding the count of abnormally behaving animals to those dead animals with detectable chlorpyrifos residues incorrectly inflates the calculated percentage of adversely affected animals.

Pages 58, 60: EFED states that neither the citrus nor turf study would support a registration requirement for chlorpyrifos use because the casualties reported from untreated sites resulted from greater search time on the untreated sites and control carcasses were not analyzed. Analyses of the casualty data presented in Fontaine (1995a, b, MRID 43706701 and 43785202 for citrus and turf, respectively) uses the casualty counts obtained during scheduled casualty searches. Since these are of equal intensity on treated and control sites there can be no effect attributable to unequal search intensity. The result from this analysis was that there was no statistical evidence for excess mortality on treated sites. Furthermore, control carcasses that could be analyzed for chlorpyrifos were analyzed, but there were no detectable residues.

Page 60: In addition to Kenaga (1968) and Clements and Bale (1988), there are other published field studies reporting the short-term effects on birds and mammals from the use of chlorpyrifos that should be added: Buck et al. (1996), Clements et al. (1992), McEwen et al. (1986), and Mullié and Keith (1993).

Page 61: "Results from terrestrial field studies in total indicate chlorpyrifos-related mortality for some species in every Class of vertebrates, including birds, small mammals, snakes, aquatic turtle, toad, and fish)." No toad in any of the three studies contained detectable chlorpyrifos. Additionally, no examples of some classes of vertebrates (e.g., agnatha and crossopterygii) were found in the three field studies.

Page 61: "In the three major field studies, few carcasses of those found were analyzed for chlorpyrifos residues (i.e., 7 out of 44 animals in the corn study, 21 out of 116 in the citrus study, and 5 out of 22 golf course turf studies)." All carcasses that were found in a condition suitable for residue analysis were analyzed.

Page 61: "Based on the time to death in the acute oral studies, affected non-target wildlife would have ample time to move far offsite or hide in the field and adjacent habitats before dying." Since neither time to death nor the time evolution of the symptoms of exposure is presented either here or anywhere else in the science chapter, this speculation about the behavior of potentially exposed animals is entirely unsupported by data. (Appendix F2)

3. Incident Reports

Page 61: "According to Huang et al. (1994), the toxicity of diazinon and chlorpyrifos are considered additive, at least in aquatic tests." This reference is inappropriate and should be removed for the following reasons: (1) The Huang et al. reference is an unpublished abstract. The work has not been validated. (2) The work was done with one aquatic organism; no terrestrial animals were tested. (3) Huang et al. state that, "A mixture of chlorpyrifos, diazinon, and methidathion produced additive toxicity to mysids." They do not present data that suggest additive toxicity to terrestrial wildlife with chlorpyrifos and diazinon as the EFED science chapter asserts (see pp 32, 61, 97, 102, 207).

Page 62: (1) "In the three field studies, researchers assumed that if chlorpyrifos residues were present, then the animal had been affected by chlorpyrifos." This is an oversimplification of the casualty classification scheme presented in all three studies. (2) The first three paragraphs are incident reports of geese killed after applications of chlorpyrifos and diazinon. The fourth paragraph is an incident involving six waterfowl where chlorpyrifos and carbofuran are identified as present. It should be noted that both diazinon and carbofuran are more toxic to birds (especially waterfowl) relative to chlorpyrifos (Hill and Camardese, 1984; Hudson et al.,1984).

The inference that the combination of chlorpyrifos and diazinon or chlorpyrifos and carbofuran cause additive toxicity is unfounded. (3) The third set of incidents were cited in Smith (1987) but reported in EPA Hazard Evaluation (1981). (4) The last sentence of the last paragraph is misleading; it should be deleted or moved to the next paragraph.

Pages 62-63: The last five incident reports have no references. (Appendix F.3)

G. Correction of Risk Quotients

1. Description of Examples

In order to determine whether higher tier ecological risk assessment is warranted for chlorpyrifos, risk quotients must be evaluated for correctness and compared to EFED's levels of concern. Dow AgroSciences has discovered numerous errors in the risk quotients presented in the EFED draft science chapter and intends to provide corrections for all erroneous values during the 60-day public comment period. For this 30-day response document, Dow AgroSciences will restrict its comments to correcting risk quotients for three example use patterns that represent major agricultural and non-agricultural uses of chlorpyrifos.

Corrections were made for numbers of applications and use rates, terrestrial and aquatic toxicity, and terrestrial and aquatic exposure. In some cases where the methods used by EFED were inappropriate, more appropriate methods were substituted to make the corrections. Details are provided in Appendix G.

In the following table the correct ("new") and incorrect ("old") risk quotients are presented for the three illustrative cases: at-plant, T-band application in field corn, aerial foliar application in alfalfa, and ground spray to turf.

67/> 3200 > 5500

2. Corrected Risk Quotients

Estuarine Invert. Reproduction NOEC

Risk Quotient New/Old Turf Surrogate Species¹ Corn Alfalfa $Mammalian \ Herbivores \ LD_{50} \quad (15 \ g \ body \ wt.)$ **0.018 - 0.82**/0.10 - 1.6 **0.023 - 1.1**/5.6 - 9.9 **0.016 - 0.76**/3.9 - 6.9 (35 g body wt.) **0.012 - 0.57**/0.071 - 1.1 (1000 g body wt.) **0.003 - 0.13**/0.016 - 0.26 **0.004 - 0.18**/0.88 - 1.6 Mammalian Insectivores LD₅₀ (15 g body wt.) 0.033/0.10 - 0.93 0.04/0.62 - 5.6 (35 g body wt.) 0.023/0.071 - 0.65 0.03/0.43 - 3.9 **0.007**/0.097 - 0.88 (1000 g body wt.) **0.005**/0.016 - 0.15 **0.005 - 0.24**/0.14 - 1.2 Mammalian Granivores LD₅₀ (15 g body wt.) 0.004/0.023 **0.004 - 0.17**/0.097 - 0.88 (35 g body wt.) **0.003**/0.016 < 0.001 - 0.034/0.019 - 0.18 (1000 g body wt.) <0.001/0.003 **0.004 - 0.18**/0.43 - 0.76 Mammalian Subacute Dietary LC₅₀ **0.003 - 0.13**/0.008 - 0.13 **0.50 -23**/57 - 100 Mammalian Reproduction NOEL **0.38 - 17**/1.1 - 17 Mammalian Acute LD₅₀ (15 g body wt.) **0.45**/1.1 (35 g body wt.) **0.19**/ 0.50 (1000 g body wt.) 0.007/ 0.018 Avian Acute Oral LD₅₀ (27.7 g body wt.) **0.47**/6.1 Avian Subacute Dietary LC50 **0.015 - 0.69**/0.077 - 1.2 **0.020 - 0.92**/4.2 - 7.4 **0.20 - 9.3**/23 - 58 Avian Reproduction NOEL **0.15 - 7**/0.42 - 6.7 **0.09**/1.9 **0.12**/16 Freshwater Fish Acute LC₅₀ **0.85**/2.0 0.18/2.5 - 4.6 **0.35**/26 - 45 Fish Reproduction NOEC **1.3**/3.0 - 5.5 **0.73**/290 **0.55**/ 34 Aquatic Invertebrate Acute LC50 **5.3**/36 **1.6**/35 - 65 **3.3**/370 - 640 Freshwater Invert. Reproduction NOEC 11/52 - 78 **0.23**/ 3.5 **0.31**/30 Estuarine Fish Acute LC₅₀ **2.2**/3.7 **0.36**/5.0 - 9.3 **0.71**/52 - 91 Estuarine Fish Reproduction NOEC **2.5**/6.1 - 11 **7.0**/ 97 Estuarine Invertebrate Acute LC₅₀ **67**/ 100 **9.3**/830

33/>300 ->570

233/> 370 > 680

¹Estuarine algae not a surrogate species of concern for assessing adverse effects of an organophosphorous insecticide

In general, the corrected risk quotients are substantially lower than the overly conservative risk quotients calculated by EFED. However, for some organisms, particularly some aquatic species, certain risk quotients still exceed levels of concern. Section III of this commentary discusses the significance of LOC exceedences for screening level assessments in the context of a tiered risk assessment procedure. It then describes the sound science necessary to refine ecological risk assessments for products that do not pass the earlier screening levels.

III. Refinement of Ecological Risk Assessments

A. Use of Risk Quotients in a Tiered Assessment Procedure

All of the ecological risk assessments presented in the draft EFED science chapter were conducted at a screening level, with weight-of-evidence analysis restricted only to those few studies and incident reports selectively chosen to support the conclusion of LOC exceedences (not a true weight-of-evidence approach that evaluates all available data to generate a probabilistic characterization of risk). However, EFED utilizes the Tier I and II risk assessments and incomplete weight-of-evidence evaluation to characterize risk from chlorpyrifos use and to compare the relative risk of chlorpyrifos use to risk associated with use of other insecticide products. This application of screening level assessments to make definitive risk characterizations runs counter to the recommendations of the Aquatic Risk and Mitigation Dialogue Group (ARAMDG), which states in its final report that a refinement of both the effects and exposure profiles beyond screening levels is necessary to characterize the actual risk posed by a pesticide product (SETAC, 1994).

The U.S. EPA FIFRA SAP also has serious concerns over the lack of probabilistic assessment approaches and the reliance on the use of risk quotients in EFED's ecological risk assessment activities (U.S. EPA, 1996c). Further, these concerns cast significant doubt on the validity of any comparative risk assessments based on RQs such as the corn cluster and the LOC Project. The corn cluster was cited repeatedly in the draft EFED science chapter and the LOC Project results were summarized in "Appendix VI. Comparison of Chlorpyrifos to Other High Risk Pesticide"

LOC's for Selected Crops based on Typical Use Rates." Both of these documents portray chlorpyrifos use as possessing greater risk than that posed by competitive products.

Specific language used in the SAP report expressing their concerns over the use of risk quotients follows in quotations from U.S. EPA (1996c):

In the studies presented for its review [corn cluster and carbofuran], the Panel is surprised that steps recommended by the New Paradigm task force (See, for example, the Aquatic Dialogue Group: Pesticide Risk Assessment and Mitigation, 1994 booklet) were not followed more closely, and/or that gaps in the process were not more clearly identified.

In the Corn Cluster Project the data gaps are such that the Agency is still trapped in a deterministic mode rather than providing rough probabilistic assessments for the chemicals concerned.

Specific Concerns:

- 4. Risk Quotient: The Panel would like to know the scientific justifications for comparing the Risk Quotient to the LOC. There are scientific questions as to the validity of both parts of the ratio.
- 7. Environmental Fate and Risk Assessment Models: How up-to-date are the environmental fate models? What research has been done to validate them with site-specific information? Are the risk assessment models applied consistent with the probabilistic approach and represent state-of-the art modeling science?
- 13. Weight of Evidence: The Panel recommends that, at a minimum, the weight of evidence parameters include at least:(a) Validated Risk Quotients (b) Chemical Properties (c), use parameters (d) Formulations (e) Field Studies, (f) Incident Data (g) Slopes of the Dose-Response-Curves to adequately provide a Tier I assessment. In addition, the Panel also recommends that the Risk Quotient be reexamined as to its theoretical justification and field test validation.

EPA's own FIFRA SAP advises EFED that without validation for quantitative prediction accuracy, the RQ methodology is suspect and should not be used for any purpose other than to screen pesticides into the higher tiers of risk assessment where true risk can be assessed, as recommended by ARAMDG.

Dow AgroSciences also notes that EFED's use of most-sensitive species LC₅₀ values and worst-case modeled exposure concentrations for RQ calculation is at odds with a 1992 EPA guidance document on risk characterization (Habicht, 1992), which states that:

A worst-case scenario refers to a combination of events and conditions such that, taken together, produces the highest conceivable risk. Although it is possible that such an exposure, dose, or sensitivity combination might occur in a given population of interest, the probability of an individual receiving this combination of events and conditions is usually small, and often so small that such a combination will not occur in a particular, actual population.

Use of single-point RQs in the EFED document presumes that these simple values characterize or quantitate risk to organisms in complex natural ecosystems, an assumption which has yet to be proven for the RQ values calculated for chlorpyrifos. It has been demonstrated that the fate and exposure level of a pesticide will depend considerably on the physical, chemical, and biological properties of the ecosystem into which the compound is introduced, and this Tier I system does not take into account the significant interactions that exist between organisms and their biotic and abiotic environment (Cairns, 1983; Kimball and Levin, 1985).

Dow AgroSciences agrees with this view of environmental toxicology and advocates refinement of the chlorpyrifos ecological risk assessments wherever correctly calculated risk quotients exceed EFED's screening levels of concern.

B. Need for Higher Tier Refined Assessment

1. Corrected RQs Exceed LOQs

In the earlier section presenting examples of corrected risk quotients, Dow AgroSciences determined that although the new quotients indicate lower risk, certain values still exceed EFED screening levels of concern.

In addition to calculating the examples of corrected risk quotients for this response document, prior to receiving the EFED draft science chapter Dow AgroSciences performed similar screening

level risk assessments using U.S. EPA OPP EFED methodology as well as higher tier regional aquatic assessments (Appendix C.1). After reviewing these screening level and regional aquatic assessments, Dow AgroSciences independently concluded that a higher assessment tier was necessary to determine actual potential risks, as recommended by ARAMDG (SETAC, 1994). Dow AgroSciences is disappointed that EFED did not progress beyond the screening level of assessment, once levels of concern were identified for chlorpyrifos.

2. Guidance Documents for Ecological Risk Assessment

As a general approach to risk assessment for chlorpyrifos, Dow AgroSciences advocates the principles described in the EPA ecological risk assessment framework (U.S. EPA, 1992b), proposed guidelines (U.S. EPA, 1996d), and final guidelines (U.S. EPA, 1998). The principles set forth in these EPA guidance documents are endorsed by the Society of Environmental Toxicology and Chemistry (SETAC, 1998) and Cal/EPA (OEHHA, 1998). The final guidelines (U.S. EPA, 1998) define a formal, stepwise assessment process involving continual communication between risk managers and risk assessors. These steps include problem formulation, analysis (characterization of exposure, characterization of ecological effects), and risk characterization. All assumptions and uncertainties in available data are explicitly stated. The intermediate Tiers, II and III, of the assessment process make use of probabilistic approaches, while the highest, Tier IV, could include special tests such as mesocosms, specialized field studies, etc.

3. Expert Panel Ecological Risk Assessments

In order to obtain refined, unbiased assessments based on sound science, Dow AgroSciences assembled two expert panels of independent academic scientists and consultants to conduct the best aquatic and terrestrial ecological risk assessments possible with existing data.

The aquatic panel conducted a comprehensive assessment, following the proposed EPA guidelines (U.S. EPA, 1996d), and building on the recommendations of ARAMDG (SETAC, 1994) and the examples of atrazine (Solomon et al., 1996) and diazinon (Novartis, 1997). The scope of the

aquatic assessment was broad, evaluating all chlorpyrifos use patterns in the 48 contiguous states. Emphasis was placed on the Midwestern corn belt because this is an important chlorpyrifos use region and the most robust surface water monitoring data was available from this area. Overall, the aquatic expert panel concluded that existing data do not suggest ecologically significant risks, except in a few locations. In addition to providing a more realistic risk characterization, this assessment identified the specific geographic areas of possible concern. This allows more efficient application of limited resources to conduct further, more site-specific assessments.

The report of the aquatic expert panel was submitted to EPA on November 18, 1998 (Giesy et al., 1998) and has been accepted for publication (Giesy et al., in press).

As a follow-up to the recommendations of the aquatic expert panel, Dow AgroSciences is conducting additional studies at some of the few locations identified as potentially experiencing ecologically significant risks. A site-specific monitoring study and risk assessment in the San Joaquin Valley of California was submitted on December 2, 1998 (Poletika and Robb, 1998). Detailed monitoring data were combined with the hazard profile described in Giesy et al. (1998) to characterize the probability of ecological risk at this site where there is heavy chlorpyrifos use. No significant adverse ecological effects were predicted.

The terrestrial expert panel assessed the potential effects of chlorpyrifos on terrestrial wildlife (Kendall et al., 1998, MRID 44709402). The panel incorporated the U.S. EPA's deterministic methodologies, as well as more recent probabilistic and modeling approaches. The fundamental construct of the assessment followed the EPA proposed guidelines (U.S. EPA, 1996d). Within this context, the environmental properties and fate, pathways of exposure, and the toxicity of chlorpyrifos in terrestrial ecosystems were thoroughly reviewed. The assessment endpoint was the potential for widespread and repeated mortality of terrestrial wildlife, particularly birds and mammals that may utilize corn agroecosystems. The panel concluded that

"... based on the weight of the evidence and available data, including a probabilistic assessment, modeling, analysis of field studies, incident reports, and extensive

scientific literature review, . . . we can rebut the presumption that the use of chlorpyrifos in corn agroecosystems will result in widespread and repeated mortality of terrestrial wildlife, particularly birds and mammals."

Methods developed in the terrestrial assessment for corn agroecosystems are also applicable to assessing risk from any other chlorpyrifos use pattern. Additional terrestrial assessments can therefore be conducted for other specific chlorpyrifos uses, if necessary. However, Dow AgroSciences believes that the conclusion reached for risk to terrestrial organisms from chlorpyrifos uses in field corn will also apply to all other chlorpyrifos uses of granular and sprayable products.

Dow AgroSciences expects EFED to review the expert panel ecological risk assessments and subsequent similar assessments and utilize the findings to refine the screening level assessments presented in the draft science chapter.

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Appendix A: Chlorpyrifos Label Use Patterns

A1. Agricultural Uses

EPA identifies several uses and use rates that seem to be driving the risk assessments. Several of these assessments are based on use patterns and use rates which contain significant errors as well as errors in interpretation of labeled use directions.. In addition, many of the assessments use scenarios constructed that have little, if any, relevancy to typical use of chlorpyrifos in agricultural production systems.

Throughout the document, EFED references BEAD quantitative use information for chlorpyrifos to develop scenarios of "typical use" on several crops. Dow AgroSciences agrees with the approach of conducting risk assessments for both typical and worst case scenarios developed from use information, although EFED's approach to identifying "typical use" is flawed. EFED has constructed "typical use" on a given crop from average application rates and average number of applications per year presented in BEAD usage information. Typical use should represent the most commonly applied rate, application method and number of applications per season for a given crop system within the context of labeled use as implemented by users of the product. This is not an average of use data.

A discussion of errant use characterization data and use pattern information for chlorpyrifos in the draft EFED science chapter document is provided below.

A.1.1. Errors in Use Data

A.1.1.2 Agricultural Use Overview (pp 6-7)

The characterization of chlorpyrifos agricultural uses on page 6 is out of date and inaccurate. The more recent BEAD data (BEAD, 1998) is a more accurate portrayal of chlorpyrifos use since it reflects significant shifts in major markets that have occurred over the past four years. Dow AgroSciences has commented on the BEAD use data and generally agrees with the overall accuracy of the information.

Based on available pesticide survey usage information for 1987 through 1996, an annual estimate of chlorpyrifos' total domestic usage is approximately 20,762,000 lb active ingredient (a.i.) for 7,916,000 acres treated. Most of the acreage is treated with 2.3 lb a.i. or less per application and 3.9 lb a.i. or less per year. Approximately equal amounts of chlorpyrifos are used in agricultural applications compared to non-agricultural applications (10,070,000 lb a.i. vs. 10,692,000 lb a.i., respectively). Chlorpyrifos is an insecticide with its largest agricultural markets in terms of total pounds a.i. allocated to corn (55%), cotton (6.8%), citrus (5.8%), apples (5.6%) and alfalfa (5.9%). No other crop is treated with more than 2.4% of the total pounds of chlorpyrifos applied. Crops with a high percentage of their total U.S. planted acres treated include apples (44%), broccoli (41%), brussels sprouts (33%), and cauliflower (31%).

The statement on page 7 regarding ranking of crop uses needs to be corrected: Use on corn represents 55% of the total volume of chlorpyrifos applied as agricultural uses. The next six major crop uses (and percent total agricultural volume) are cotton (6.8%), citrus (5.8%), apples (5.6%), alfalfa (5.9), pecans (2.4%) and wheat (2.1%). Crops other than corn are grouped into similar chlorpyrifos usage and sites (e.g., cover crops with reduced soil erosion, such as alfalfa, etc.).

A.1.1.3 Corn

The EFED document contains information on page 110 in reference to chlorpyrifos corn uses that is out of date and inaccurate. This information should be corrected with more current BEAD use information as follows: Chlorpyrifos is primarily applied to corn as a granular formulation and liquid formulation for a total of about 7% (8% is the likely maximum) of the 71,264M acres of corn in the U.S.

A.1.1.4 Alfalfa

The usage data for chlorpyrifos on alfalfa in the EFED document (p 131) should be updated. Most recent BEAD estimates (BEAD, 1998), which agree with Dow AgroSciences' estimates, are that chlorpyrifos is applied to an average of 3% (maximum 3%) of the 23,949M acres of

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4.9% of agricultural

alfalfa grown in the U.S. Alfalfa accounts for 480M lb a.i. of annual use (4.9% of agricultural use) which places it in the top five crops for chlorpyrifos usage. California, Pennsylvania, Missouri, Illinois, Kansas and Colorado account for 55% of the use of chlorpyrifos on alfalfa. Average use is one foliar application at 0.7 lb a.i./A.

A.1.1.5 Wheat

The EFED science chapter states (p 139) "although chlorpyrifos is currently applied to only about 1 percent (likely maximum of 2 percent treated) of the 71,464,000 acres of wheat fields in the U.S., the use is new and the amount of treated acreage is likely to increase dramatically." The reality is the Section 3 registration for Lorsban 4E-SG insecticide was granted in 1993; prior to this most of the states for which Lorsban 4E-SG is registered exercised Section 18 emergency exemptions annually since the late 1980s. Use is not likely to "increase dramatically" but rather remain within 100M to 400M lb a.i. used annually depending on occurrence of outbreaks of Russian wheat aphid, orange wheat blossom midge and grasshoppers. The most recent BEAD usage data for chlorpyrifos indicates that chlorpyrifos is applied to an average of 1% (maximum 1%) of the 64,081M acres of wheat grown in the U.S. Texas, Colorado Kansas, Wyoming, Montana, North Dakota, Minnesota and New Mexico account for more than 90% of the 279M lb a.i. of chlorpyrifos annually applied to this crop. Average use is 1.2 applications made to winter wheat at an average rate of 0.6 lb a.i./A.

A.1.1.6 Peanuts

Use of chlorpyrifos on peanuts has substantially declined during the last four years due to the registration of DMI fungicides for control of white mold. Average annual use of chlorpyrifos on peanuts is now estimated at 119M lb a.i., with applications between 4% and 8% of the 1,610M acres of peanuts in the U.S. (BEAD, 1998).

A.1.1.7 Cotton

The usage data for chlorpyrifos on cotton in the EFED document (p 148) should be updated. Most recent estimates (BEAD, 1998), which agree with Dow AgroSciences' estimates, are that chlorpyrifos is applied to an average of 5% (maximum 6%) of the 12,429M acres of cotton grown in the U.S. Cotton accounts for approximately 670M lb a.i. of annual use (6.8% of agricultural

use), which places it as the second highest crop for chlorpyrifos usage. Average use is 1.7 foliar applications at 0.6 lb a.i./A.

A.1.1.8 Tobacco

Use of chlorpyrifos on tobacco is significantly overestimated in the description of use in the EFED document (pp 153-154). Most recent estimates (BEAD, 1998) are that chlorpyrifos is applied to an average of 11% (maximum 14%) of the 695M acres of tobacco grown in the U.S. North Carolina, South Carolina, Virginia and Georgia account for 81% of the 146M lb a.i. of chlorpyrifos annually applied to this crop. Average (and typical) use is one pre-transplant application of Lorsban* -4E insecticide at 2.0 lb a.i./A.

A.1.1.9 Sorghum

Use of chlorpyrifos on sorghum is overestimated in the EFED science chapter (p 157). According to the most recent estimates (BEAD, 1998), chlorpyrifos is applied to an average of 2% (maximum 3%) of the 11,280M acres of sorghum grown in the U.S. Average use is 1.1 application at 0.6 lb. a.i./A. The states of Texas, Mississippi, Kansas, Oklahoma, Nebraska and Louisiana account for 76% of chlorpyrifos applied to sorghum.

A.1.1.10 Soybeans

Use of chlorpyrifos on soybeans as a percent of acres treated is significantly overestimated three-to ten-fold in the EFED science chapter (p 159). According to the most recent estimates (BEAD, 1998), chlorpyrifos is applied to an average of less than 1% (maximum <1%) of the 61,279M acres of soybeans grown in the U.S. Average use is one application at 0.7 lb a.i./A applied to an average of 90M to 150M acres compared to EFED's reported estimate of 290M to 1,520M acres. Illinois, Iowa, Ohio, South Dakota, and Indiana account for 53% of chlorpyrifos applied to soybeans.

A.1.1.11 Sunflowers

Use information for chlorpyrifos on sunflowers needs to be updated in the EFED science chapter (p 162). According to the most recent estimates (BEAD, 1998), chlorpyrifos is applied to an

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average of less than 1% (maximum <1%) of the 2,745M acres of sunflowers grown in the U.S. Average use is 1.1 applications at 0.7 lb a.i./A applied to an average of 7M to 130M acres. Minnesota, Colorado, California and Kansas account for 81% of chlorpyrifos applied to sunflowers.

A.1.1.12 Vegetables

The EFED science chapter states chlorpyrifos use on vegetable crops represent less than 1% of the total chlorpyrifos poundage on agricultural crops. This information is out of date based on the most recent estimates (BEAD, 1998) of chlorpyrifos use and on current market trends. Use of chlorpyrifos on brassica vegetable crops (broccoli, cauliflower, cabbage, etc.) represents nearly 1.2% of the total poundage of chlorpyrifos applied to vegetable crops. Although foliar applications to these crops are still important for control of aphids and Lepidoptera, the withdrawal of fonofos from the market in 1997 has created an increased demand for chlorpyrifos for control of soil pests such as root maggots in brassica and symphylans in tomatoes and asparagus in the western U.S.

A.1.1.13 Citrus

Citrus use information for chlorpyrifos reported in the EFED science chapter (p 170) is out of date and inaccurate. According to the most recent estimates (BEAD, 1998), chlorpyrifos is applied to oranges on about 14% (19% likely maximum) of the 867M acres, grapefruit on 12% (16% likely maximum) of the 194M acres; lemons on 30% (43% likely maximum) of the 63M acres and other citrus (including limes, tangelos and tangerines) on 16% (32% likely maximum) of the 51M acres. Most chlorpyrifos use on citrus occurs in California with significantly lower usage in Arizona, Texas and Florida.

A.1.1.14 Fruit and Nut Orchard Applications (Dormant, Foliar, Trunk and/or Soil Floor)

Use information for fruit and nut orchard applications for chlorpyrifos reported in the EFED science chapter (page 170) is out of date and inaccurate. Dow AgroSciences' estimates that dormant fruit and nut uses (including directed trunk applications) represent approximately 340M lb a.i. of annual usage which would rank this use as the fifth highest agricultural use.

The EFED science chapter states that "according to BEAD, apples are the highest use crop for chlorpyrifos in this category with treatment of 53 percent of 452,000 acres (likely maximum use is 63 percent of the acreage)." The most recent estimates (BEAD) for chlorpyrifos use on apples is 44% (53% likely maximum) on 572M acres accounting for an average use of 550M lb a.i. per year. It is important to note that the BEAD estimates do not differentiate dormant from foliar applications. Dow AgroSciences estimates that approximately 300M lb a.i. are applied to apples as a dormant or delayed dormant application as Lorsban-4E insecticide and 250 lb a.i. are applied as foliar post-bloom applications as Lorsban* 50W insecticide.

The current BEAD data also estimates use on pecans at 29% (36% likely maximum) of 488M acres accounting for 143M lb a.i.; use on almonds at 20% (29% likely maximum) of 429M acres accounting for 88M lb a.i.; and use on walnuts at 30% (39% likely maximum) of 205M acres accounting for 62M lb a.i. It should be noted that although the BEAD estimates for percent acres treated for almonds and walnuts agree with Dow AgroSciences estimates, the total pounds active applied to these crops is substantially lower than Dow AgroSciences estimates.

A.1.2 Errors in Labeled Uses

A.1.2.1 Corn

The EFED science chapter references four granular formulations that can be applied to corn (pp 105, 120). Risk assessments for agricultural uses of granular formulations of chlorpyrifos should only be conducted on the 15% clay-based granular formulations, such as Lorsban* 15G granular insecticide. The 0.5% and 1% granular formulation registrations are registered for use as home and garden products only and have little or no relevance in risk assessments focused on agricultural use. Both of these low concentration granules have no practical utility in commercial corn production. The Lorsban* 7.5G insecticide registration has never been commercialized as a product and will not be supported in the reregistration of chlorpyrifos.

The EFED document indicates that at-plant granular applications of chlorpyrifos may be applied as a band, T-band or in-furrow at 1.2 to 2.4 oz a.i. per 1000 feet of row (p 121). A maximum rate of 2.4 oz a.i. per 1000 feet of row is used in the EFED risk assessment conducted for at-plant granular banded corn use (p 123). This maximum use rate is incorrect. The maximum use rate for all at-plant applications of Lorsban 15G insecticide on corn is 1.2 oz a.i. per 1000 feet of row.

A table that summarizes application rates on corn, number of applications and minimal time interval between treatments is presented on page 106 of the EFED document. This table is incorrect based on the above information. A corrected version of this table is presented below:

Corrected Corn Use Pattern Summary Table (p 106)

Application Type and Application Method	Chlorpyrifos Formulation	Application Rates (expressed as ai)	Maximum Number of Applications	Maximum lb ai/A per Season	Treatment Interval (days)
Seed Treatments: Stored Seeds: Preplant Seed::	50 % WP	1 oz. ai./100 lbs. of seed 1 oz. ai./100 lbs. of seed	1	NA NA	NA NA
Pre-plant: Broadcast (Soil Depth of Incorporation)	4 EC (2-4") 15 G (4-6")	1 lb/A in \geq 10 gal./A 2 lb/A in \geq 10 gal./A 3 lb/A in \geq 10 gal./A 1 lb/A 2 lb/A	1 1 1 1 1	NA NA NA NA	NA NA NA NA NA
At Plant: Broadcast	4 EC	1 lb/A in \geq 20 gal. 2 lb/A in \geq 20 gal.	1 1	NA NA	NA NA
At Plant: Soil Band soil incorporated 0.5 to 2" deep (15% available)	0.5 G 1 G 7.5 G 15 G (6-7" wide) (6-7" wide) (7-10" wide)	NA NA NA 1.2 oz/ 1,000 ft.	1 1 1 1 1 1	NA NA NA NA NA NA	NA NA NA NA NA NA
At Plant: In-furrow (1% available)	15 G (assume 6" wide)?	1.2 oz/ 1,000 ft.	1 1	NA NA	NA NA
Preemergence: Broadcast	4 EC	0.5 lb/A in \geq 20 gal. 1.0 lb/A in \geq 20 gal.	1 1	NA NA	NA NA
Cultivation: Sidedress	4 EC 15 G	1 lb/A 0.9 oz/ 1,000 ft. 1.2 oz/ 1,000 ft.	1 1 1	NA NA NA	NA NA NA

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Application Type and Application Method	Chlorpyrifos Formulation	Application Rates (expressed as ai)	Maximum Number of Applications	Maximum lb ai/A per Season	Treatment Interval (days)
Postemergence:	4 EC	0.25 lb/A in 20-40 gal.	1		
Broadcast	4 LC	0.23 10/A III 20-40 gai.	2	7.5 lb/A	as needed
(ground spray		0.5 lb/A in 20-40 gal.	1	7.10 10/11	as needed
in 20-40 gal.)		č	2	7.5 lb/A	as needed
or		1 lb/A in 20-40 gal.	1		
(aerial spray			2	7.5 lb/A	as needed
in sufficient water)		1.25 lb/A in 20-40 gal.	1		
		1.5.11-/4 :- 20.401	2	7.5 lb/A	as needed
		1.5 lb/A in 20-40 gal.	2	7.5 lb/A	as needed
(ground & aerial)	15 G	0.75 lb/A	1	7.5 IU/A	as needed
(ground & acriai)	15 G	0.75 10/11	2	2.025 lb/A	as needed
		0.975 lb/A	1		
			2	2.025 lb/A	as needed
Sweet Corn:	4 EC	0.5 lb/A	22	11 lb/A	as needed
(FL & GA only)	(aerial 2 gal.)	1 lb/A	11	11 lb/A	"
Broadcast	4 EC	0.5 lb/A	22	11 lb/A	"
	(ground)	1 lb/A	11	11 lb/A	"

A.1.2.2 Clover Grown for Seed

The chlorpyrifos use pattern scenario described for maximum chlorpyrifos uses on clover grown for seed is both incorrect and agronomically impossible (pp 135-136). Lorsban-4E insecticide is labeled for control of garden symphylans prior to establishment of the crop as a pre-plant broadcast application at a rate of 2 lb a.i./A. Lorsban-4E insecticide is also labeled as a foliar spray application at 1 lb a.i./A. The EFED science chapter assessed both of these applications occurring within the same season with a 14 day treatment interval and assessed the foliar spray application at a rate of 2.0 lb a.i./A, 2X the maximum labeled rate. Clover is a perennial crop established either in the spring in combination with a companion crop (such as a small grain) or direct seeded in late summer. A foliar treatment would not occur in the same season as crop establishment. In fact, the 14 day treatment interval is unreasonable based on the fact that germination and establishment of hard seeded legumes such as clover can take two to four weeks. Therefore, maximum use should be assessed as a single pre-plant broadcast application incorporated to a depth of 2-4 inches, or as a single foliar broadcast application at a rate of 1.0 lb a.i./A. In addition, it should be noted that clover grown for seed is only labeled for use in Oregon (SLN OR-940031).

The EPA included rapeseed (canola) in the cover crops category (Group 2) and includes a risk assessment for rapeseed uses based on a maximum use rate of 1 lb a.i./A and 6 foliar with 7 day intervals between applications (pp 137-138). There is no existing labeled use or tolerance for chlorpyrifos on rapeseed in the U.S., nor is there a pending tolerance petition for chlorpyrifos on rapeseed. In addition, no Section 18 label for chlorpyrifos on rapeseed were found in a search of all existing and expired Section 18 registrations in the U.S.

A.1.2.4 Cotton

The section in the EFED science chapter that examined use of chlorpyrifos on cotton was confusing and inaccurate. In addition to a seed slurry treatment for cotton seed and a gin trash treatment, use of chlorpyrifos on cotton is restricted to foliar broadcast applications of Lorsban-4E or Lock-On* insecticides at rates of 0.1875 - 1.0 lb a.i./A with a maximum of six applications allowed per season. All foliar uses in all states fall within this use pattern description.

EFED described and conducted a risk assessment for a pre-plant incorporated broadcast spray at 1 lb a.i./A limited to the state of Mississippi (pp 148-149). However, no registration (Section 3, Section 24(c) or Section 18) exists for any Dow AgroSciences chlorpyrifos-based product as a pre-plant soil treatment. Additionally, chlorpyrifos is not currently registered for use on cotton in Mississippi.

The assessment for maximum post plant applications at 0.5 lb a.i./A limited to Alabama and Mississippi (pp 150-151) is confusing since chlorpyrifos is not registered for use in Mississippi and the maximum foliar use allowed in Alabama is 1.0 lb a.i./A.

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A.1.2.5 Soybeans

The EFED preliminary risk assessment makes reference to a use of chlorpyrifos on soybeans at 0.5 lb a.i./A limited to Indiana, Michigan and Ohio. This is a reference to SLNs granted in 1988 for use of Lorsban 50W insecticide on soybeans. These SLNs expired in December of 1988.

A.1.2.6 Vegetables

Use of chlorpyrifos on mushrooms referenced in the EFED document (p 166) was discontinued in 1988 and will not be supported through reregistration.

A.1.2.7 Fruit and Nut Orchard Applications (Dormant, Foliar, Trunk and/or Soil Floor)

The EFED document references on page 179 that "directions for chlorpyrifos use on registered labels are for a single, dormant treatment to be sprayed by ground or <u>aerial</u> equipment at 0.5 lb ai/100 gallon (200-600 finished spray/A) on almonds, apples, nectarines, peaches, pears, plums and prunes." This is incorrect as the Lorsban-4E insecticide label clearly states that dormant applications based on these dilution rates are to applied by ground equipment. A Special Local Needs registration allows for aerial application of 2 lbs a.i./A to almonds and walnuts could be construed to cover dormant applications (SLN CA-940017). Thorough coverage and penetration of tree bark is critical for dormant applications to be effective. This can only be achieved by ground application equipment. It is unlikely that a certified Pest Control Advisor in California would recommend aerial application of dormant applications. Thus, the maximum dormant tree use of 3.0 lb a.i./A must be assessed as a ground application and not as an aerial application (p 180).

The reference to use of chlorpyrifos on macadamia nuts in Hawaii as a foliar treatment is incorrect (p 180). This use is a directed trunk spray of Lorsban 50W insecticide for control of ambrosia beetles, not a foliar application (SLN HI-930011).

A.1.3. Errors in Interpretation of Use Data, Label Information and Typical Use

A.1.3.1 Corn

Risk assessments are conducted on "typical corn use" in two states, Iowa and Mississippi, as an "update" to assessments conducted in the corn cluster (pp 128-129). The EFED document states "according to BEAD, the typical use rate on corn is a single pre-plant, granular application at an average of 1.1 lbs. a.i./A." This information is incorrect as it represents a misinterpretation of the largest and most important agricultural use pattern for chlorpyrifos in the U.S. The typical use pattern for chlorpyrifos on corn in all areas of the U.S. is a single at-plant, T-Band application of Lorsban 15G insecticide at a rate of 1.2 oz a.i. per 1000 feet of row.

A.1.3.2 Alfalfa

EFED assessed typical use as a single foliar aerial application at 0.7 lb a.i./A (pp 133-134). Typical use is a foliar aerial application at 1.5 pt of Lorsban-4E insecticide per acre (0.75 lb a.i./A).

A.1.3.3 Cranberries

Cranberries were included in the Fruit and Nut Orchard Applications category vegetables category (Group 6). Dow AgroSciences believes this to be an inappropriate categorization of this use pattern. Based on common agricultural production practices for this crop, it is more appropriate to include cranberries in cover crops (Group 2). Cranberries are a low growing perennial crop with a dense canopy. Although EFED expressed concern over flooding and drainage of chlorpyrifos treated cranberry bogs into freshwater and estuarine areas, this concern is unfounded. Cranberry bogs are only flooded in the fall prior to harvest as a harvest aid. Chlorpyrifos treatments are applied in the summer. In fact, because cranberry bogs are contained within a dyke and soils are highly organic in nature, runoff into adjacent bodies of water would be unlikely.

A.1.3.4 Grass Grown for Seed

Although the maximum chlorpyrifos use pattern scenario described in the EFED science chapter for grass grown for seed (pp 136-137) is theoretically permissible by Lorsban-4E insecticide,

Special Local Needs labeling in Oregon and Nevada (SLN OR-940032 and SLN NV-940002, respectively), the presumed treatment interval of seven days is highly contrived. Lorsban-4E insecticide is labeled for control of billbugs, cutworms and aphids in perennial grass seed crops in these two states. Billbugs are controlled with treatments (1.0 lb a.i./A) typically applied in April. Control of cutworms with 1.0 lb a.i./A typically occurs in April/May or in the late fall. Aphids are also a cool weather pest with treatments at a lower rate of 0.5 lb a.i./A in the spring or fall. It is unlikely that two consecutive treatments of Lorsban-4E insecticide would occur with less than a 30-day treatment interval. Additionally, the probability that a field would receive more than one application of Lorsban-4E insecticide per season is extremely low.

A.1.3.5 Mint

Mint was included in the vegetables category (Group 4). Dow AgroSciences believes this to be an inappropriate categorization of this use pattern. Based on common agricultural production practices for this crop, it is more appropriate to include mint in cover crops (Group 2). Mint is a perennial crop with a growth habit similar to forage crops, such as alfalfa, which forms a dense canopy over the field. The crop is also harvested in a manner similar to forage crops and insecticide application methods are also similar to those made to forage crops.

A.1.3.6 Wheat

The maximum and typical wheat use patterns assessed for chlorpyrifos were appropriate; however, the EFED science chapter makes no mention of the required buffer zones and application restrictions for ground and aerial applications of Lorsban 4E-SG insecticide (EPA Reg. No. 62719-245). For aerial application, the Lorsban 4E-SG insecticide label states "Do not apply by air within 300 feet of aquatic habitats (including lakes, public reservoirs, rivers, permanent streams, marshes, natural ponds, estuaries or other natural waters)." For ground applications, the Lorsban 4E-SG insecticide label states "For ground applications, the distance from treated areas to aquatic habitats (including lakes, public reservoirs, rivers, permanent streams, marshes, natural ponds, estuaries or other natural waters) must be 30 feet or more." In addition, a general use restriction on the label states "Do not apply product where runoff is likely to occur to aquatic habitats (including lakes, public reservoirs, rivers, permanent streams,

marshes, natural ponds, estuaries or other natural waters)" and "Do not apply when weather conditions favor drift or runoff from treated areas."

Assumptions concerning edge of field runoff and spray drift deposition based on above aquatic risk mitigation labeling must be appropriately considered in assessing risk to non-target aquatic and terrestrial organisms. Such use restrictions have been incorporated in a probabilistic risk assessment submitted by Dow AgroSciences (Havens, 1995); however this work is not referenced in the EFED document.

A.1.3.7 Peanuts

Typical use of chlorpyrifos on peanuts is described in the EFED science chapter (p 142) as a "single at-plant, granular application at an average of 1.8 lbs. a.i./A." At-plant applications do not represent the typical use of chlorpyrifos on peanuts; rather, typical use is a post-plant ground applied band application of Lorsban 15G insecticide made at the early pegging stage of growth at 2.25 oz a.i. per 1000 feet of row (2.0 lb a.i./A). The assessment conducted for typical chlorpyrifos application to peanuts should be recalculated based on this information.

A.1.3.8 Cotton

The use of a three-day spray interval assessment of the maximum use rates and six applications to cotton is highly contrived with an extremely low probability of repeat applications at this spray interval ever occurring. A seven-day spray interval for two applications with the 1.0 lb a.i./A might possibly occur under heavy beet armyworm pressure. A worst case, yet unrealistic, six application scenario might involve one to two applications for early season use (May-June) at low rates (0.1875 - 0.5 lb a.i./A) for control of plant bugs followed by one to two applications in July at 0.5 - 0.75 lb a.i./A for control of boll worms or aphids (typically in a tank mix) and one to two applications in late season (August-September) at 1.0 lb a.i./A for control of armyworms.

Dow AgroSciences agrees with the EFED assessment of the typical use of chlorpyrifos on cotton represented by one application per season. However, a typical use rate of 0.75 lb a.i./A is more appropriate than 0.5 lb a.i./A utilized in the EFED assessment. This is due primarily to a

significant shift in use from the Southern U.S. and Arizona cotton markets to California where 0.75 lb a.i./A is a commonly applied rate.

A.1.3.9 Tobacco

EFED assessed the typical tobacco use as a single pre-transplant ground spray application at 2.2 lb a.i./A; however, 2 lb a.i./A is a more appropriate typical use rate. Dow AgroSciences submitted a probabilistic risk assessment that evaluated the use of chlorpyrifos on tobacco (Havens and Peacock, 1995), but this work was not referenced in the EFED document.

A.1.3.10 Sugarbeets (and Sugarbeets Grown for Seed)

Sugarbeets (and sugarbeets grown for seed) were included in the vegetables category (Group 4). Dow AgroSciences believes this to be an inappropriate categorization of this use pattern. Based on common agricultural production practices for this crop, it is more appropriate to include sugarbeets in field crops (Group 3).

Sugarbeets represent an important use for chlorpyrifos, representing 1.6% of the total agricultural consumption and placeing it in the top ten crops by use. According to the most recent BEAD estimates (BEAD, 1998), chlorpyrifos is applied to about 8% (10% likely maximum) of the 1,415M acres of sugarbeets grown in the U.S. Average use is 1.5 applications at 0.9 lb a.i./A. applied to an average of 118M - 146M acres. California, North Dakota and Minnesota account for 86% of chlorpyrifos applied to sugarbeets. Surprisingly, no risk assessment for this important use was reported in the EPA EFED draft science chapter even though Dow AgroSciences submitted a probabilistic risk assessment for this use in 1995 (Havens and Peacock, 1995).

Two formulations of chlorpyrifos are registered for use on sugarbeets, Lorsban 15G granular insecticide and Lorsban-4E insecticide. Lorsban 15G may be applied at a <u>maximum use rate</u> of 1.35 oz a.i./1000 ft of row (equivalent to 2.0 lb a.i./A, based on standard 22-inch row spacing). Lorsban 15G is applied principally as an at-plant T-Band. Post-emergence banded applications up to 2 - 4 leaf stage of plant growth are allowed by the label, but seldom, if ever, used since liquid

applications are preferred for post-emergence applications. Only one application of Lorsban 15G insecticide may be made per year to sugarbeets.

Lorsban-4E insecticide may be applied as a pre-plant or at-plant incorporated band and as a post-emergence band or broadcast application. A <u>maximum use rate</u> of 2 pt/A (1.0 lb a.i./A may be applied with a <u>maximum of four applications</u> per season allowed.

<u>Typical use</u> for chlorpyrifos on sugarbeets differs with two geographically distinct use areas. Typical use of chlorpyrifos in sugarbeets grown in the Red River Valley of North Dakota and Minnesota involves <u>either</u> an at-plant T-Band application of Lorsban 15G insecticide at 1.0 lb a.i./A <u>or</u> one application of Lorsban-4E insecticide at 1.0 lb a.i./A applied as a post-plant band by ground application equipment or broadcast by air. Typical use of chlorpyrifos in irrigated sugarbeet production in California involves one application of Lorsban-4E insecticide at 1.0 lb a.i./A applied by air.

A.1.3.11 Citrus

EFED references BEAD information on average applications and use rates as being typical citrus uses (one foliar airblast application to oranges at 2.4 lb a.i./A). This is incorrect because this information reflects market research averages on a national basis and does not take into account significant geographical differences in use. The typical use of chlorpyrifos on citrus is a single foliar airblast application to oranges in California at 6.0 lb a.i./A for control of California red scale. Chlorpyrifos is only registered for ground application in California.

A.1.3.12 Fruit and Nut Orchard Applications (Dormant, Foliar, Trunk and/or Soil Floor)

The treatment interval of seven days specified for maximum almond and filbert foliar uses (p 181) is highly improbable. Two treatment windows exist for foliar use of chlorpyrifos on almonds: (1) a single foliar application in May targeted at second generation peach twig borer; and, (2) an application in late July or early August (1% hull split) targeted at third generation peach twig borer and potentially navel orange worm. If navel orange worm is the target, a second application

14 days later might possibly be made, although chlorpyrifos is typically not used for both applications against navel orange worm.

The treatment interval of seven days specified for maximum almond orchard floor use is highly improbable. Two applications are allowed in almond orchard floors because there are two times in the year where these treatments are effective. A treatment may be applied in spring when mounds become active to reduce overall ant population density in the orchard. A second treatment window is prior to harvest to reduce direct feeding damage by ants on nuts which dry on the orchard floor following shaking. At least a 60-day treatment interval would be more appropriate.

A.2. Non-Agricultural Uses

A review of the non-agricultural use patterns described in the draft EFED science chapter uncovered a number of errors, both in specific information, which was conveyed incorrectly, and by virtue of omission. Additional information would have provided a more complete, balanced picture of the overall perceived risks associated with the currently labeled application of chlorpyrifos in non-crop uses. Dow AgroSciences' comments on non-agricultural uses will be organized by use pattern.

A.2.1 Termiticides/Perimeter Applications Corrections

1. The draft EFED chapter stated on pages 6, 42 and 97 that "The highest concentration of chlorpyrifos applied as a non-agricultural use of 2,000 to 5,000 ppm as a perimeter spray application around structures following a termite treatment." To be correct, this statement should be changed to reflect that the highest concentration of chlorpyrifos allowed for labeled non-agricultural uses would be the application of a 2% (20,000 ppm) concentration. This application is associated with (1) underground utility cable and conduit preventative termite treatments; (2) utility pole and fence post termite treatments; and, (3) both pre-construction and post construction termite control when used in accordance with the variable volume termiticide use directions for selected visible applications. In these variable volume uses, the

professional applicator may apply up to a 2% dilution of chlorpyrifos, but must only use one-half of the typical application volume to the specified target site. While this option is available on the label, the typical termiticide treatment is made using a 7,500-10,000 ppm solution applied to the specified target site(s) using long-established industry standard volumes described on the termiticide label.

- 2. The draft EFED chapter implied on pages 6, 42 and 97 that "perimeter spray application around a structure" follows a "termite treatment," and on pages 201-202 that it would "control termites and other pests up to 15 feet from the house." According to Dow AgroSciences product labels (Dursban* Pro specialty insecticide, Dursban* 50W specialty insecticide, Empire* 20 specialty insecticide, Dursban* TC specialty termiticide concentrate and Equity* specialty termiticide concentrate), a perimeter treatment is described as a labeled application of chlorpyrifos-containing products around structures to control such insects as "ants, bees, beetles, boxelder bugs, carpenter ants, centipedes, clover mites, cockroaches (numerous species), crickets, earwigs, elm leaf beetle adults, fire ants, fleas, flies, hornets, millipedes, mosquitoes, pillbugs, scorpions, sowbugs, spiders, springtails, ticks, wasps, yellowjackets," and other outdoor pests. It is important to note that the linkage implied between termite control and perimeter pest control is not correct. As shown above, termites do not appear on any of our products as an approved insect for which a perimeter treatment may be made.
- 3. The indication on pages 201-202 of the draft EFED science chapter that these perimeter applications would control pests "up to 15 feet away from the structure" is also incorrect. The use directions for perimeter applications using high volume (up to 10 gal/1000 sq ft), low concentration (0.03% 0.12%) dilutions of chlorpyrifos can be made to "a band of soil 6 to 10 feet wide around and adjacent to the structure, also the building foundation to a height of 2 to 3 feet, where pests are active and may find entrance." As such, the distance away from the structure where pests may be controlled is only 10 feet, instead of 15 feet, as specified in

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the draft EFED science chapter. It is also important to note that our Dursban Pro, Dursban 50W and Empire 20 labels also provide use directions for perimeter applications using low volume, high concentration dilutions by applying the product(s) to "specific areas such as cracks and crevices along walkways, patios, windows and door frames or other areas where insects may congregate or can gain entrance to the structure." This low volume, high concentration application may be made using a low pressure system, such as a one gallon hand pump sprayer and chlorpyrifos dilutions up to 0.5% (5,000 ppm). The Dursban TC specialty termiticide concentrate and Equity specialty termiticide concentrate labels provide similar directions for perimeter applications to control the same pests (not including termites) cited above by diluting any leftover termiticide in their spray tank to a 0.25% - 0.5% (2,500-5,000 ppm) dilution and applying it as "a band of soil 6 to 10 feet wide around and adjacent to the structure, also the building foundation to a height of 2 to 3 feet, where pests are active and may find entrance." The intent of this label language was to allow a small professional applicator (with a single spray tank) to be able to make a termiticide application, and to also legally use any remaining product to control perimeter pests, either at the same structure or a subsequent structure, without having to completely empty and clean their tank to mix a Dursban Pro specialty insecticide dilution for use as a perimeter treatment.

- 4. The statement made on page 194 of the draft EFED science chapter that "A formulation of 0.03 to 0.06 percent (30,000 to 60,000 ppm ai) may be made with 10-20 gallons used per structure and treated 1 to 4 times per year." is incorrect. A 0.03 0.06% solution would equate to a 300 600 ppm solution a difference of over two magnitudes from the values calculated by the EPA.
- 5. The reference to "micro-encapsulated granules" on page 194 of the draft EFED science chapter as a formulation that is approved for use as a perimeter treatment is also incorrect. Dow AgroSciences does not have registered a granular micro-encapsulated product; our micro-encapsulated formulation is a liquid suspension of chlorpyrifos that has been

encapsulated resulting in 15-20 micron particles suspended in water when diluted. As such, Dow AgroSciences has no knowledge on a micro-encapsulated granular formulation.

6. The EFED science chapter goes on to state on page 194 that "Applications (mostly homeowner use) of a 1.7 to 12% concentrate diluted by 10-30 gallons per structure yields chlorpyrifos levels as high as 12,000 ppm ai in water." This is also incorrect in that the maximum dilution is 1.2% (12,000 ppm). The more typical application concentration is 2,800 ppm - 3,700 ppm.

A.2.2 Turf Applications Corrections

- 1. The draft EFED science chapter stated on pages 6-7, 199 and 200 that "According to chlorpyrifos labels, agricultural application rates range from a minimum of 0.25 lbs ai per acre for wheat to a maximum of 8 lbs ai per acre per application for lawns and up to 11 lbs ai per acre per season for sweet corn in Florida and Georgia." It is important to note that the 8 lb rate identified in the draft EFED chapter as being applied to "lawns" is not for residential use; it is only used on sod farms for fire ant control where quarantine certification is required prior to shipment of sod outside of the quarantine area. All other turf applications are at a maximum of 4 lb a.i./A, with the vast majority applied at 1 lb a.i./A.
- 2. On pages 18-19 of the draft EFED chapter, the model used to calculate the number of granules per LD₅₀ assumes that Lorsban 15G granular insecticide is formulated on corn cob. It has not been for at least 15 years! It is formulated on a clay carrier. Homeowner products, such as Dursban* ½G granular insecticide and Dursban* 1G Insecticide can be formulated on corn cob, as well as clay and other materials. Therefore, in order to calculate a more representative number of granules/LD₅₀ with a chlorpyrifos granule formulated on corn cob, it would have to be done with Dursban ½G and Dursban 1G. This would result in a 15-30 fold increase in the number of granules/LD₅₀, resulting in a change in the table found on pages 19-20. Therefore, the 29 granules/LD₅₀ for the house sparrow should be changed to a range of 435 870 granules/LD₅₀.

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- 3. The draft EFED chapter states on page 44 that, "Since chlorpyrifos has been demonstrated to be very highly toxic to birds, testing was requested for two types of granular formulations: Dursban ME 20 (a microencapsulated clay-coated granular formulation) and Lorsban 15G (a 15% granular agricultural formulation)." As stated above (see Termiticide/Perimeter Application Corrections (A.2.1) # 5) Dursban* ME20 Microencapsulated Insecticide is not a granular formulation.
- 4. The draft EFED science chapter states on pages 193-194 that, "Risk quotients estimated in the following two tables assume maximum application rates of chlorpyrifos on golf course turf (i.e., two applications of 4 lbs ai/A each for both spray and granular formulations at a minimum interval between applications of 30 days)." Only liquid spray products are applied at a maximum of 4 lb a.i./A. Granular products are applied at a maximum of 2 lb a.i./A followed by a second application of 2 lb a.i./A after two weeks. Both of these maximum use rates are for the control of grubs in turf.

A.2.3 Ornamental Applications Corrections

- 1. The draft EFED science chapter states on pages 191-192 that, "Directions for homeowner use on ornamentals on registered labels permits chlorpyrifos to be sprayed with a 1.7% to 12% concentrate diluted with 15 to 30 gallons of water in hose-end sprayers. ... According to the label instructions, the treatment concentration may be as high as 8,000 ppm (i.e., 120,000 ppm / 15 gallons = 8,000 ppm)." The actual highest concentration applied according to the labels is 1% (10,000 ppm) dilutions used for beetle control (10 2/3 oz/ gal). The vast majority of ornamental uses are applied at 600-1200 ppm.
- 2. The draft EFED science chapter states on page 7 that "homeowner fruit trees are [treated with] up to 4.0 lbs ai/A." As the chlorpyrifos products labeled for homeowner fruit trees direct the trees to be "sprayed to run-off," it is unclear how the EPA developed their estimate

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of 4.0 lb a.i./A. To allow Dow AgroSciences to fully comment, the rationale used to develop this treatment rate will need to be fully disclosed.

3. The application rate cited on page 192 in the draft EFED science chapter for "Homeowner use on fruit, nut and citrus trees are sprayed at 0.25-2 lbs ai/100 gallons (1-4 lbs ai/A)" is incorrect. The rate of application would be 0.25-3 lb a.i./100 gal. As mentioned in Ornamental Application Corrections #2 above, it is unclear how the EPA developed their estimate of 1-4 lb a.i./A. To allow Dow AgroSciences to fully comment, the rationale used to develop this treatment rate will need to be fully disclosed.

A.2.4 Pet Shampoo Corrections

The draft EFED science chapter stated on page 9 that, "Risks for indoor uses have not been assessed for wildlife effects, but some uses, such as the pet shampoos used at kennels and pet grooming shops, have aquatic risks in biomonitoring studies. Pet shampoos have been identified in effluents from some publicly owned treatment works (POTW, i.e., sewage treatment facilities) as the source of chlorpyrifos in effluents that exceed discharge permit levels and are toxic to *Ceriodaphnia*, an aquatic invertebrate used in biomonitoring." Prior to publication of the draft EFED science chapter, Dow AgroSciences, in cooperation with the U.S. EPA and all other manufacturers of chlorpyrifos, voluntarily removed chlorpyrifos from all pet shampoos and pet dips. We are uncertain why these deleted use patterns were referenced in the draft EFED science chapter.

A.2.5 Mosquito Control Corrections

The draft EFED science chapter states on pages 203-204 that, "ULV Mosquito Master 412 is a mixture of 12% chlorpyrifos (90 lbs/gallon) and 4% permethrin (30 lbs/gallon) for use by public health officials as well as trained personnel." Based on our knowledge of chlorpyrifos, it is MPOSSIBLE to develop a 12% chlorpyrifos formulation which is 90 lb/gal! While not an expert on permethrin, it also seems highly unlikely that a 4% permethrin mixture would also contain 30 lb permethrin/gal.

A.2.6 Ornamental Applications Differences in Interpretation

In the draft EFED science chapter on pages 191-192, the statement is made that "Ornamentals are sprayed to runoff. Description of use rates as 'apply to runoff' is not quantifiable and poses a problem for calculating EECs....The following table estimates the number of spray drops equal to the LD50 values and non-standard, risk quotients for select avian and mammalian species drinking one (1) drop of the spray solution......The 8,000 ppm aqueous spray exceeds the levels of concern for most terrestrial animals based on only the consumption of only one drop." Dow AgroSciences takes exception to the method of risk quotient (RQ) calculation for perimeter and ornamental applications. Spray to runoff is when the spray material just begins to drip off of the foliage. This amount when hitting the ground would not be expected to puddle to where a bird or other animal could easily drink any. As such, the RQs calculated using the technique employed by EFED would be extremely over-conservative and, in many cases, would not accurately reflect risks posed by the applications being modeled.

Appendix B: Chemical and Environmental Fate Properties

B.1 Chemical Profile (p 10)

B.1.1 Errors

The physico-chemical properties presented here are correct, although the structures presented in Appendix I are in error. The structures shown are for O-ethyl O-(2,4,6-trichloro-2-pyridinyl)phosphorothioate and 2,4,6-trichloropyridine. The correct structures are:

$$\mathsf{(CH_3CH_2O)_2} - \mathsf{P} - \mathsf{O} - \mathsf{N} - \mathsf{CI}$$

chlorpyrifos (O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl)phosphorothioate

TCP (3,5,6-trichlorpyridinol)

B.2 Aerobic Soil Metabolism (p 12)

B.2.1 Errors

The table which appears on page 13 entitled "Soil Degradation Half-lives (in months) Rates Under Different Conditions" has several errors. Upon examination of the original citation (Racke et al., 1994), the following errors were found:

10 μg/g, Florida soil, 25° C, Medium Water: **15 months, not 115 months**. 100 μg/g, Florida soil, 15° C, High Water: >**24 months, not 22 months**.

100 μg/g, Florida soil, 25° C, High Water: **7 months, not 3 months**.

1000 μg/g, Florida soil, 25° C, Medium Water: >25 months, not >24 months.

B.2.2 Uncited Studies and Omissions

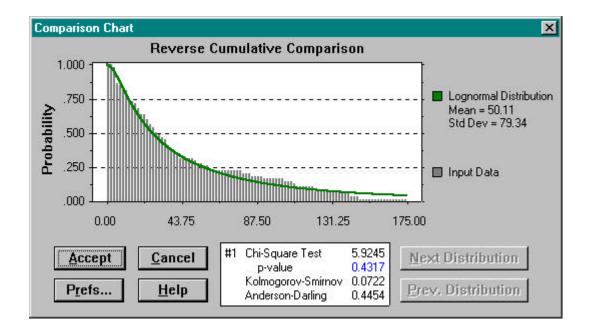
Applying the input selection rules for GENEEC employed by the FIFRA Model Validation Task Force and draft EFED guidance (R.D. Jones, April 1998) for the studies cited in the document (Bidlack, 1977 and Cranor, 1990) the conservative t ½ for modeling can be set at 109days. This value is achieved by the following formula:

$$t^{1/2} = \text{mean} + (t_0 * \sigma)/\sqrt{n}$$

where t_{90} is the student's t statistic for 0.1 confidence at n degrees of freedom and σ is the standard deviation of the data. In this case, the mean = 78 days, t_{90} = 1.397, n = 8, and σ = 63.

However, the document fails to cite the extensive body of work on laboratory degradation of chlorpyrifos which appears in the open literature, as well as additional Dow AgroSciences submissions. This information was thoroughly reviewed and summarized by Racke (1993). From the information in this reference, chlorpyrifos applied to soil at agricultural rates degraded with first-order half-lives of 3.8 - 145 days (discounting studies performed under air-dry soil conditions and at termiticidal rates). Applying similar input rules for, t ½ can be set at 53.2 days (mean = 45 days, $t_{90} = 1.298$, $t_{90} = 1.298$,

The above method assumes that the distribution of the data is well-described by the student's-t probability distribution. As this is not necessarily true, a different approach to determining the 90th percentile value for model input involves attempting to fit other continuous probability distributions through the data. One way to do this is through the use of computer tools such as Crystal Ball (Decisioneering, Inc.). The choice for distribution type are lognormal, weibull, gamma, exponential, pareto, extreme value, beta, logistic, normal, triangle, and uniform. A lognormal distribution provided the best fit for the chlorpyrifos soil degradation half-lives as shown below.



Sampling 5000 times from this distribution yields a 90th percentile value of 109 days. Thus, the appropriate model input value for aerobic soil degradation is in the range of 53 - 109 days. The most conservative value to use is likely 109 days, while a more typical value would be about 53 days.

The study which is used to set the longest aerobic half-life of 180 days (Cranor, 1990) is not a Dow AgroSciences-performed study. A search of the NPIRS/EPA PDMS database revealed that the study was submitted by Makhteshim Chemical Works, Ltd., a generic manufacturer of chlorpyrifos. The quality and/or applicability of this data point cannot be determined by Dow AgroSciences within the timeframe of this response. The cited follow-up study on the degradation of TCP (MRID 42144912) was also submitted by Makhteshim Chemical Works and could not be evaluated.

At termiticidal rates, chlorpyrifos does have the potential to be more persistent, as pointed out in the document. The mean of the half-lives in the cited reference (Racke et al., 1994, summarized in Racke, 1993) is about 400 days. Using the t-statistic method, the 90th percentile is about 680 days.

B.3 Aerobic Aquatic Metabolism and Aquatic Dissipation (pp 13, 27)

B.3.1 Uncited Studies and Difference in Interpretation

This document states that these data are not needed to support the labeled uses of chlorpyrifos; however, this sort of information is used in the aquatic exposure characterization and subsequent risk assessment. In response to a data call-in of September 18, 1991, Dow AgroSciences submitted a study (Kennard, 1996, MRID 44083401) which concluded that the aerobic aquatic half-life of chlorpyrifos in pond water, kept in the dark, is about 30 days. In this study, TCP attained a maximum level of 44% of the applied dose, or 19.4 ppb, in the water phase.

The dissipation of chlorpyrifos in aquatic systems has been extensively reported, both in the literature and in Dow AgroSciences unpublished reports. The document states that "the shortest half-life of chlorpyrifos in water in 29.6 days" (p 27). The source of this figure is unreferenced.

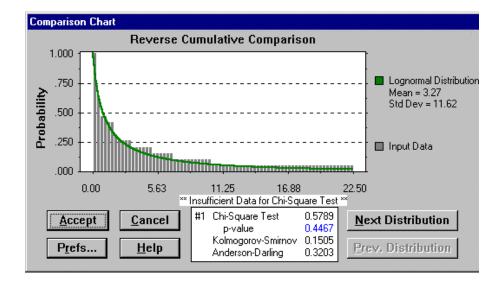
The more complete data set can be employed to refine the inputs for modeling of the aquatic fate of chlorpyrifos as well as aid in the quantification of uncertainty. The table below summarizes this information.

Summary of Chlorpyrifos Dissipation in Aquatic Systems

Source	Conditions	Reported $t_{1/2}$ or DT50 (Days)	t _{1/2} Used in Probability Distribution
Reimer and Webster (1980)	Artificial Pond	0.21	0.21
Reimer and Webster (1980)	Artificial Pond	0.58	0.58
Leeuwangh (1989)	Artificial Pond	1 to 2	1.5
Huges et al. (1980)	Artificial Pond	< 0.08	0.08
Huges et al. (1980)	Woodland pond	< 0.08	0.08
Knuth and Heinis (1992)	Pond (littoral enclosure)	0.33	0.33
Knuth and Heinis (1992)	Pond (littoral enclosure)	0.26	0.26
Knuth and Heinis (1992)	Pond (littoral enclosure)	0.2	0.2
Lungle (1988)	Pond (littoral enclosure)	0.3-1.7	1
Lungle (1988)	Pond (littoral enclosure)	1.7-2.4	2.05
Zulkifli et al. (1983)	Rice Paddy	0.6	0.6
Zulkifli et al. (1983)	Rice Paddy drainage pond	0.3	0.3
Schaefer and Dupras (1970)	Sewage effluent holding pond	1.67	1.67
Cryer and Robb (1995)	Farm pond	6.7	6.7
Cryer and Dixon-White (1995)	Farm pond	5.1	5.1
McCall et al. (1984)	Farm pond	3	3
Siefert et al. (1989), Brazner et al. (1989), Brazner and Kline (1990); Knuth and Heinis (1992)	Lake (littoral enclosure)	4.7 - 8.0 hr	0.265
Garg and Sethi (1980)	Rice Paddy	10	10
Kennard (1996)	Aerobic Aquatic Metabolism	30 (kept dark)	30

Using the half-life values from these studies and again applying the EPA input selection rules (R.D. Jones, April 1998), the overall t $\frac{1}{2}$ for modeling should be set at 5.5 days. In this case, the mean = 3.4 days, $t_{90} = 1.328$, $t_{90} = 1.328$

Again employing a log-normal fit of these data points, the following fit was achieved:



The distribution shown was sampled 5000 times to obtain a smoother distribution, yielding a 90th percentile for the aquatic dissipation half-life for chlorpyrifos of 7.08 days. Thus, a value in the range of 5.5 - 7.08 days is a more appropriate model input value for the aerobic aquatic half-life for chlorpyrifos based upon guidance by EPA guidelines for the selection of model inputs (USEPA, 1995a), where 90th percentile values (10% exceedence) for dissipation half-lives are suggested.

B.4 Field Dissipation (pp 14-15)

B.4.1 Errors

The information cited from a Florida citrus dissipation study is not correctly listed. Half-lives of 27 - 32 days extracted from the report are not half-lives, but times to non-detectable residue levels (0.1 ppm). For these particular trials, half-lives could not be calculated due to the non-first-order behavior of the dissipation. Half-lives of 1.3 - 19.9 days have more certainty, as is discussed in the report. The referenced maximum TCP levels could not be extracted from the original report; upon examination of the original data tables, maximum levels of TCP (in the top 6 inches of the soil column) were very low, all less than 0.2 ppm; in the top 1 inch of soil, and the maxima ranged up to 1.8 ppm, one day after the third application. Estimation of day 0 chlorpyrifos concentrations was complicated by fast abiotic hydrolysis of the parent to the TCP metabolite in the dry soil.

The referenced MRID 40356608 (McKellar, 1984) is a method for the residue analysis of the herbicide triclopyr and its degradate TCP in soil. It does not appear that this citation is relevant to the section in which it appears.

B.4.2 Omissions

The other two field studies are cited correctly, although it should be noted that TCP levels reached maxima of 50% and 58% of applied in the corn and turf studies, respectively (Fontaine et al., 1987 [MRID 40395210] and Racke et al. 1993a, 1993b [MRID 42924801, 42924802]).

A large body of additional field dissipation work was excluded from consideration in the document; the studies are extensively reviewed in Racke, 1993. Over 40 different field experiments are cited on a wide variety of crops, management practices, and formulations. Excluding application of granular formulations at very high rates, half-lives were generally less than 60 days, with a minimum of four days reported.

B.5 Sorption K_{oc} (pp 13-14)

B.5.1 Omissions

The document cites the core sorption/desorption studies and a roughly mean value is employed for modeling. However, the document fails to note the larger body of literature on the sorption of chlorpyrifos as summarized by Racke (1993). A more appropriate mean value to use for GENEEC and PRZM-EXAMS modeling is 8500 mL/g. However, instructions received with the SCI-GROW program (M. Barrett) indicate that it is appropriate to use the <u>median</u> value, at least for SCI-GROW modeling; this is about 6000 mL/g.

B.5.2 Modeling Input for Chlorpyrifos — Differences in Interpretation

As can be seen above, there is extensive literature information available on the environmental fate of chlorpyrifos. The table below summarizes the analysis performed above and gives recommended values for modeling parameter input values.

Property	EPA value used for exposure modeling	Updated Value (from analysis above)
Solubility	2 ppm	no change
Hydrolysis t ½	72 days	no change
Photolysis t ½	29.6 days	no change
Aerobic soil	180 days (GENEEC)	109 days (GENEEC)
metabolism t ½ (ag	75.9 days (PRZM-EXAMS)	53 days (PRZM-EXAMS)
rates)	63 days (SCI-GROW)	109 days (SCI-GROW)
Aerobic soil	506 days	400 days (SCI-GROW)
metabolism t ½		
(termiticidal rates)		
Aerobic aquatic	0 days (stable)	7.08 days (lumped
metabolism t ½		degradation rate)
K_{oc}	6070 ml/g	8500 (GENEEC and PRZM-
		EXAMS)
		6000 (SCI-GROW)

B.6 Environmental Fate Properties of TCP

The environmental chemistry of the principal degradate of chlorpyrifos, 3,5,6-trichloropyridinol (TCP) is not addressed in the Fate and Transport section of the document. However, environmental fate properties of this chemical are extensively used as inputs into the modeling that is used to set estimated exposure levels in water. As pointed out in the document, TCP is also the primary degradate for the Dow AgroSciences herbicide triclopyr, so there are additional references cited below which were submitted as part of the reregistration process for triclopyr.

B.6.1 Solubility — Error

The document lists solubility at pH 2.5 as 117 mg/L and increasing at higher pH to 500 mg/L. Examining the original source of this data (Meikle and Hamaker, 1981), the solubility at relevant pH is much higher; the authors list the solubility of the dissociated sodium salt of TCP at pH 7 to be 49,100 mg/L.

B.6.2 Hydrolysis t ½ — Differences in Interpretation

In the chlorpyrifos hydrolysis study cited, TCP did indeed accumulate and did not appear to degrade by hydrolytic processes. It is unclear, however, why a t ½ value of 180 days was chosen by the Agency. Barring further information, it is recommended to assume that TCP is stable to hydrolysis (i.e., set the t ½ to 0 in GENEEC).

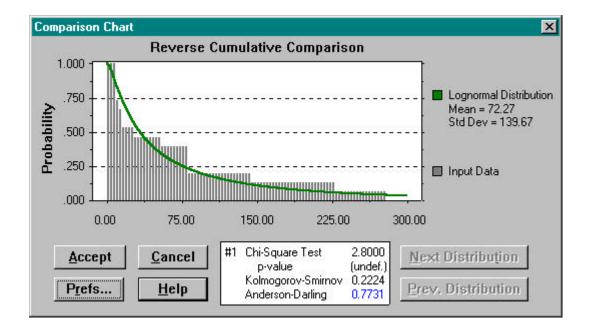
B.6.3 Photolysis t ½ — Uncited Study

The document sets this at one day, based on soil photolysis. However, there are specific data measuring the photolytic breakdown of TCP in solution. An early study (Smith, 1966) appeared in the literature showing 50% degradation in less than two hours (0.08 days) and complete photolysis in 10 hours. In another study, Dilling et al. (1984, MRID 00095241) also reported complete photolysis in ten hours. As a conservative estimate, the photolysis t ½ can be set at one day for modeling purposes.

B.6.4 Aerobic Soil Metabolism t ½ — Uncited Study

The document estimates the range of soil degradation half-lives from the core chlorpyrifos soil metabolism study. Estimates of the range of t $\frac{1}{2}$ values are listed as ranging from 65 - >360 days and then a multiplier is applied to estimate the t $\frac{1}{2}$ to be 600 days. This methodology is not documented and is inconsistent with Agency modeling guidance. Much more usable data has been submitted by Dow AgroSciences; a study specifically studying the degradation of TCP in 15 soils was submitted (Bidlack, 1977, MRID 00095381). Using the half-life values from this study and again applying the EPA input selection rules (R.D. Jones, April 1998), the conservative t $\frac{1}{2}$ for modeling should be set at 99 days. In this case the mean = 69, t_{90} = 1.341, n = 15, and σ = 85.

A lognormal probability distribution also was fit to these data, yielding the following fit:



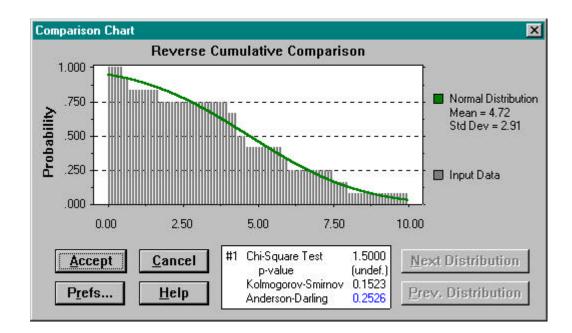
A sample of 5000 points from this distribution gave a 90th percentile t ½ value of 166 days.

Thus, the appropriate input for more refined modeling should be in the range of 99 - 166 days.

At termiticidal rates, it is indeed likely that degradation of TCP will be very slow, as TCP has been shown to have fungicidal and bacteriostatic properties (Racke and Robbins, 1990).

B.6.5 Aerobic Aquatic Metabolism t $\frac{1}{2}$ — Uncited Study and Differences in Interpretation The Kennard study (1996) showed the continued accumulation of TCP in an aerobic aquatic system, held in the dark. However, field information taken from triclopyr direct applications to lakes and static ponds (report in preparation), indicates that TCP does not accumulate in aquatic systems, likely by a combination of photodegradation and/or metabolism. For modeling purposes, a "lumped" degradation t $\frac{1}{2}$ of six days can be employed, provided that the photolysis and hydrolysis rate constants are set at zero. In this way, the field observations, incorporating all processes, including photolytic attenuation, uptake, dilution, and metabolism, can be incorporated into the exposure assessment. The six-day value also is calculated by the FIFRA Model Validation Task Force methodology described above (mean = 4.7 days, t = 1.356, n = 12, σ = 2.9 days).

Fitting a truncated normal probability distribution to these data gives the following comparison chart:



The 90th percentile of this distribution is about 8.5 days, so a reasonable value for model input is between 6 and 8.5 days.

B.6.6 K_{oc} — Differences in Interpretation

The document chooses the geometric mean value for K_{oc} from the 1990 Racke and Robbins study (1990, MRID 41892802). However, instructions received with the SCI-GROW program (M. Barrett) indicate it is appropriate to use the <u>median</u> value, at least for SCI-GROW modeling. In addition, there is another acceptable study on sorption/desorption of TCP (Racke and Lubinski, 1992, MRID 42493901). If both studies are considered, the median K_{oc} is 151 mg/L.

B.6.7 Model Input for TCP — Differences in Interpretation

As can be seen above, the body of literature on TCP is quite extensive and includes both unpublished Dow AgroSciences reports (many of which have been submitted to the Agency) and reports in the open literature. The table below summarizes this analysis.

Property	EPA value used for exposure	Updated Value (from analysis
	modeling	above)
Solubility	500 ppm	49100 ppm
Hydrolysis t ½	180 days	stable
Photolysis t ½	1 day (soil)	1 day (water)
Aerobic soil	600 days	99 days
metabolism t ½		
Aerobic aquatic	0 days (stable)	6 days (GENEEC)
metabolism t ½		8.5 days (PRZM-EXAMS)
		(lumped degradation rate)
K_{oc}	136 ml/g	151 ml/g

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Appendix C: Aquatic Exposure Profile

C.1. Aquatic Exposure Modeling

The highest predicted EEC will likely come from scenarios such as the 10:1 field/pond ratio as outlined in the chlorpyrifos RED document. However, little is done to address even U.S. EPA's own remarks for determining exposure profiles such as "What is exposed?", "How much exposure occurs?", and "When and where does it occur?" when using this simplistic approach (U.S. EPA, 1998). Having a 100% treated field draining into a stagnant water body does not address the latter two constraints proposed by U.S. EPA scientists. Since the methodology of a farm pond is used by U.S. EPA-OPP as a regulatory approach for characterizing ecological risk, an in-depth overview of physicochemical properties and model input values to estimate chlorpyrifos exposure is warranted.

A unifying theme throughout the exposure calculation resides in the lack of use of field observations. Laboratory data are often used to understand the environmental behavior under field conditions when artificially induced to only a single mechanism or dissipation pathway (e.g., hydrolysis, aqueous photolysis, etc.). Field information generally have multiple mechanism(s) occurring simultaneously. While the details of these interactions may not be totally quantifiable (or understood) based upon laboratory experiments, they do provide actual observations/measurements for field behavior for a pesticide and thus should not be omitted when attempting to predict "field" behavior of a pesticide in question using a numerical modeling tool.

Throughout the EFED document, several field studies were apparently chosen in a biased fashion to represent extreme exposure observations. It is alarming that EFED is willing to utilize field observations when adverse effects are observed, but fail to use field information/knowledge for use in model predictions as there is no basis (scientific or otherwise) for this course of action. Adverse field observations are used to corroborate GENEEC or PRZM/EXAMS simulations without any justification as to the applicability of such a comparison. Any comparison is

problematic since none of the referenced field observations resemble the 10:1 field/pond scenario used for EFED modeling, or often the typical agronomic practices found on the product label.

The use of PRZM as a tool for predicting edge-of-field runoff and leaching is being addressed by the FIFRA Environmental Model Task Force, Model Validation Work Group of the American Crop Protection Association (ACPA). It appears that PRZM is capable of predicting edge-of-field runoff within an order of magnitude when properly calibrated. The PRZM model does have limitations when forced into simulating the standard 10:1 field/pond scenario. This scenario will give the highest estimated environmental concentrations (EEC) since 1) 100% of the treated area drains directly into the pond, 2) no riparian/buffer regions exist, and 3) what happens past the field edge (e.g., pond/stream hydrodynamics) is not accounted for. In addition, landscape factors representing the orientation of the field to the pond, varying field slopes, run-out areas, terraces, etc. are not described nor geographically referenced as "different" modeling scenarios are developed. Field behavior often cannot be used as a surrogate for watershed behavior since many of the scaling factors are not 1:1 (i.e., the runoff behavior from a 10-ha field is not 1/10th as much as from a 100-ha field). As the watershed size increases, the runoff potential scaling typically decreases. Even models such as PRZM have built-in algorithms to account for sediment yields as a function of a non-linear representation for field size.

The GENEEC tool is developed from PRZM/EXAMS simulations for a 10:1 field/pond scenario. However, in GENEEC, a runoff event is forced to occur two days following a pesticide application. This may (or may not) be a real occurrence of having an upper percentile runoff producing storm immediately following a pesticide application. Since most pesticides have an application window for efficacy against a target pest species, the likelihood of having a large storm following an application is further propelled to the upper extremes in terms of the probability of occurrence by simple probability rules¹. The validity of always having a large

 $^{^1}$ If two events A and B are independent, then the probability of event A and B occurring simultaneously [P(A and B)] equals P(A) * P(B) . Since the probability of an event E [P(E)] is between 0 and 1 (i.e., $0 \le P(E) \le 1$), P(A and B) is ≤ 1 . Since extreme event probabilities are much less than 1, the joint probability would even be smaller.

precipitation event following an application needs to be addressed and quantified on a region by region and pesticide use basis before GENEEC should be employed as a screening device.

C.1.1 Correction of Errors

p 23. The word "model" should be inserted in the sentence "EFED used the GENEEC model for most uses."

p 24. "The modeling report should be consulted for more details and the cumulative frequency graphs (see Appendix IV)."

Appendix IV contains only a single page which is simply a repeat of the table found on pages 25-26. No modeling details, nor cumulative frequency graphs based upon modeling simulations, exist and replication of model runs and assumptions could not be explored. In the future, OPP would do well to follow their own suggestions for documentation of modeling information in reports as given by OPP's draft guidelines (U.S. EPA, 1993).

Table on pages 29-30, 35 should label all columns indicating a concentration with appropriate units [i.e., mg/L].

Table on page 37 needs units for concentration. Also, no mention as to what model/methodology is used to determine surface water concentrations (chronic and acute) for TCP. Should reference an appendix if appropriate.

Sentence on page 38 is not a complete sentence and the meaning is unclear: "Note: No separate exposure numbers have been calculated for this use for surface water since this is a highly localized and deeply incorporated use not as subject to surface runoff." Should this sentence be more along the lines of "Exposure estimates for surface water contamination resulting from termiticide use have not been estimated."?

On page 38 it states "However, these data (monitoring) are not targeted specifically to chlorpyrifos use areas and information on chlorpyrifos usage in the watersheds sampled from is not readily available." This information does exist [Geisy et al. 1998, and is also currently in press *Rev. Environ. Contam. Toxicol.*] which shows that several of the NAWQA watersheds are in areas of intense chlorpyrifos usage (as given by sales information).

On page 38, the heading "Acute concentration of chlorpyrifos parent in flowing waters:", the word "parent" can be removed.

p 39. "It is probably more reasonable to use the maximum monitoring value than to use the highly conservative PRZM/EXAMS generated maximum peak EEC of 31 mg/L⁻¹ (Table 5) ..."

The peak EEC value of 31 mg/L⁻¹ cannot be found in Table 5 for any of the modeled scenarios.

p 39. In the first paragraph, the section entitled "Conclusions on likely Drinking Water Exposure Levels" should be referenced as an appendix for further details.

C.1.2 Uncited Studies

C.1.2.1 Chlorpyrifos Removal from Granules

p 19. "It seems reasonable to assume the corncob granules would not decompose extremely rapidly, providing the opportunity for avian and mammalian exposure, since the chlorpyrifos half-life in soil is approximately 180 days."

A methodology to describe the chlorpyrifos release characteristics from clay granules as a function of water induced advection, diffusion, and volatilization is given elsewhere (Cryer and Laskowski, 1994, 1998). This methodology has been used to numerically estimate chlorpyrifos release rates from clay granules using Dubuque, Iowa weather and an average Iowa soil (Cryer, 1995). Advection resulting from precipitation flowing past a granule is

the mechanism responsible for the largest chlorpyrifos release from the granule into soil (73%), followed by diffusion (22%) and volatilization (5%). The predicted median release interval for all the chlorpyrifos mass within the clay granule formulation to be removed ranged from 11 - 17 days.

p 34. "It has been shown (00144906) that chlorpyrifos will leave corn watershed in Illinois and can be transported to ponds a short distance from the fields; quantities transported are generally less than 1% of the applied."

Cryer and Dixon-White (1995) summarized a comprehensive chlorpyrifos runoff field study performed in Iowa during the severe flooding of 1993. Even in a year of unprecedented precipitation, only limited amounts of chlorpyrifos were observed to leave the field in water and eroded sediment (0.38% of applied). Less severe precipitation years would most likely transport much less. In fact, in a report for the 1992 growing season (Cryer and Robb, 1995), only 0.25% of applied was observed to leave the same watershed. Also, more advanced modeling taking into account the release characteristics of Lorsban 15G granules (Cryer and Laskowski, 1998) has shown that model predictions for edge-of-field transport of chlorpyrifos is less than 1% of applied at the 99th percentile (i.e., 1-in-100 year frequency of occurrence) for representative Midwestern corn scenarios.

C.1.2.2 Granular Rate of Release

Estimated environmental concentrations (EECs) of pesticide in surface bodies of water must be determined to assess the potential exposure risk for aquatic organisms. Current runoff models (GLEAMS, EPICWQ, SWRRBWQ, PRZM, etc.) can be used to predict pesticide mass in runoff water and erosion sediment for liquid (or emulsifiable) formulations. However, these programs were not written to account for controlled-release formulations such as granules or controlled-release devices, and the use of these models for simulating the fate of granular formulations can give erroneous results unless properly accounted for.

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Chlorpyrifos must first be released into the environment before processes such as runoff and degradation become important. Diffusion release of chlorpyrifos from the clay granule matrix is assumed to be rate limited by transport mechanisms responsible for moving chlorpyrifos away from the granule surface. These mechanisms of transport include volatilization, advection, and diffusion into the surrounding soil matrix. Details of the methodology can be found elsewhere (Cryer and Laskowski, 1994, 1998). Each mechanism is treated independently to match several of the lab and field experimental observations which were used to estimate rate and diffusion coefficients, integration constants, etc. Higher level tier exposure modeling has utilized this transient release rate methodology for predicting the amount of chlorpyrifos available in soil for leaching, degradation, runoff, etc. (Havens et al. 1998; Cryer et al. 1998a) and to provide a more realistic exposure assessment for clay granule formulations.

C.1.2.3 Higher Tiered Exposure Modeling

Limitations for GENEEC and single site PRZM-EXAMS scenarios have been described elsewhere in this document. Using Tier I modeling as a starting framework, higher level tiers have been performed to address chlorpyrifos aquatic exposure in a probabilistic fashion. Probability modeling with geographic spatial resolution allows all lower tiers to be put into perspective in terms of the frequency of occurrence, in addition to pinpointing the location of vulnerability. A methodology has been proposed and implemented for a higher tiered probabilistic/mechanistic approach to address aquatic risk to non-target mechanisms. This methodology, used by Dow AgroSciences, has been reviewed and accepted in a variety of peer-reviewed scientific journals [Havens et al., 1998; Cryer et al., 1998a; Cryer and Laskowski, 1998; Cryer et al. 1998b; Cryer and Havens (accepted)].

In fact, an EPA Memorandum from Peter Caulkins (U.S. EPA, 1995b), Acting Chief of the Special Review and Reregistration Division (OPP, OPPTS) of EPA expressed such superlatives as "We are pleased with what you (Dow AgroSciences) have managed to accomplish technologically and believe that probabilistic methods greatly enhance the field of aquatic risk assessment", and "Your technological and computer capabilities are certainly leading the field in risk assessment. We hope to see more of this type of assessment in the future". Dow AgroSciences has provided

EPA with several of these aquatic Tier III probabilistic exposure/risk assessments [Havens et al. (1994); Havens and Peacock (1995); Havens 1995) for a variety of markets where chlorpyrifos is sold. These reviews indicate chlorpyrifos exposures are not as intense as indicative by Tier I modeling and can be further reduced through appropriate management practices.

C.1.3 Differences in Interpretation of Evidence

C.1.3.1 Estuary Scenario

p 27. "EECs used in the estuarine risk assessments are the same as those calculated for the farm pond, because some estuaries may be similar to farm ponds in which pesticides and sediments are readily deposited and from which little is transported out of the system."

The use of GENEEC and/or PRZM/EXAMS for estimating estuary concentrations is a blatant misuse of the model over the range in which it is valid. These models were developed specifically for a field/pond scenario of a specific geometry, etc. Therefore, any extrapolations to predict estuary concentrations are not physically based (i.e., unreliable). If such a gross exposure extrapolation is to be made, than at a minimum EFED scientists should provide error/uncertainty bounds, especially for chronic exposure values. The huge error bounds that would ensue would be indicative of the ridiculous predictions associated with an extrapolation of this nature. When EPA requested the Scientific Advisory Panel (SAP) and Science Advisory Board (SAB) to review the ARAMDG document, a comment made was "The SAP is also concerned that these approaches (farm pond scenario) and the report do not address the effects in estuarine environments" (U.S. EPA, 1995c).

An estuary is a complex ecosystem. Multiple fresh water sources (i.e., streams and rivers) continually feed the estuary. The episodic nature of pesticides in rivers would indicate that both pesticide addition and dilution can occur. In addition, tidal actions twice per day would effectively mix the water within an estuary. Monitoring information for several rivers located within regions of heavy chlorpyrifos usage indicate maximum concentrations for chlorpyrifos are in the ppt range. Thus, based upon dilution alone in an estuary, the concentration would be

orders of magnitude less than this value. It is anticipated that most estuaries will have spatially averaged exposure values far below monitored values found in streams and rivers due to the active tidal mixing between the estuary and open water and dilution effects of the estuary itself.

p 29. "In the citrus field study, two water samples collected on Day 1 tested positive for chlorpyrifos. The measured concentrations in these two water samples were 1.2 and 486 ppb, which clearly bracket all the above, modeled EEC's."

Having two data points that are two orders of magnitude different should at least signal to the reader/reviewer that something is amiss with the study, either procedurally or with the analytical methodology. Extremely high water concentrations were attributed to misapplication of chlorpyrifos, based upon labeled procedures, where chlorpyrifos was inadvertently applied directly to the surface of the pond. Details can be found in the section entitled <u>Aquatic Effects in Terrestrial Field Studies</u>. Selectively choosing information from field observations to validate Tier I modeling should be avoided unless the field study design is similar to the scenarios being modeled.

C.1.3.2 Choice of Model Input

The modeling performed by OPP could not be repeated since the majority of modeling input parameters were not specified or documented anywhere within the EFED document. Only physicochemical properties and chlorpyrifos use rates are tabulated. Soil properties, years of historical weather patterns, field geometry, field curve numbers and soil erosion parameters, etc. are lacking and, thus, PRZM-EXAMS simulations cannot be repeated. It does appear the choice of physicochemical input parameters for the terrestrial modeling are appropriate as far as single value choices go. The one parameter apparently misrepresented is the aquatic dissipation half-life for chlorpyrifos in pond water.

Using a probability density function approach for selecting the appropriate chlorpyrifos aquatic dissipation half-life from a variety of both internal reports and peer-reviewed journal articles (Appendix B) yields a value of 7.08 days.

Table E.2 summarizes EFED PRZM-EXAMS and GENEEC predictions. All of the EFED scenarios (pp 25-26) were rerun using GENEEC, both with original EFED parameters properties (aerobic aquatic half-life = infinity) and with EFED parameters but with an aerobic aquatic half-life of 7.08 days. Refined GENEEC/PRZM-EXAMS values are represented in bold, while the original EFED EECs are given as regular type. GENEEC simulations using the chlorpyrifos aerobic half-life of 7.08 days could be simulated. However, an approximation method had to be used for scaling EECs predicted by PRZM-EXAMS since these modeling scenarios could not be reconstructed using information in the draft EFED document. EFED PRZM-EXAMS simulations assumed no aerobic aquatic dissipation for chlorpyrifos (clearly incorrect). Thus, the EFED predicted EECs should be lower if one accounts for the known aerobic aquatic dissipation. Details of this scaling methodology along with results of all of the GENEEC simulations are given in this Appendix under the section "GENEEC Simulations and Techniques Used to Refine PRZM-EXAMS Simulations" (C.2).

Table E.2¹. Revised Estimates of pond water concentrations using 10th percentile chlorpyrifos aquatic dissipation half-life of 7.08 days. Draft EFED/revised values given as normal/bold type, respectively.

Site	Application	Appl. Rate	Initial	4-day	21-day	60-day	90-day
	Method	(lbs ai/A)	(PEAK)	average	average	average	average
			EEC (ppb)				
Corn - Iowa (PRZM-EXAMS)	1 ground spray	3	11.1	8.7	4.5	2.7	1.9
Marshall Silty Clay Loam	appl., incorp. 2"		10.6	7.45	2.60	0.99	0.33
Corn - foliar spray (GENEEC)	1 ground spray,	1.5	5.5	4.8	2.7		
	unincorporated		5.38	4.16	1.52	0.60	
Corn - foliar spray (GENEEC)	1 aerial appl	1.5	7.7	6.8	3.8	2.3	
			7.0	5.6	2.0	0.79	
Corn - foliar spray (GENEEC)	3 aerial appl. 14-	1.5	24	21.5	11.7	6.8	
	day interval		18	14.2	5.2	2.0	
Corn - GA spray (PRZM-EXAMS)	11 aerial, foliar	1	15.8	12.8	7.4	5.6	4.3
Cowarts Sandy Loam	appl.		11.9	8.4	3.3	1.8	0.7
Corn - granular, pre-plant (GENEEC)	1 ground appl.,	2	1.66	1.44	0.81	0.51	
	incorporated 4"		1.66	1.27	0.46	0.18	
Corn - granular, pre-plant, Iowa	1 typical ground	1.3	4	3.1	1.6	1	0.7
(PRZM-EXAMS - Corn Cluster)	appl., incorporated 4"		3.7	2.6	0.91	0.38	0.13

¹ GENEEC was re-run for all scenarios listed in this table. An approximation technique is used to estimate aquatic exposures for the PRZM-EXAMS simulations since details documenting the input parameters chosen are not provided in the draft EFED document. Details of the methodology used for approximating the refined EECs is given in Appendix A.

Corn - granular, pre-plant, Miss. (PRZM-EXAMS - Corn Cluster)	1 typical ground appl., incorporated 4"	1.3	4.6 4.2	3.7 3.1	1.9 1.1	1.1 0.42	0.7 0.13
Corn - granular, post-plant, (GENEEC)	•	2.4 oz/1000 ft of row	8.63 8.63	7.48 6.60	4.2 2.41	2.6 0.95	
Corn - granular, foliar, (GENEEC)	2 aerial appl. 14- day interval	0.975	6.35 6.35	5.5 4.86	3.1 1.77	1.9 0.7	
Citrus - Florida (PRZM-EXAMS) Adamsville Sand	2 airblast appl., 30-day interval	3.5	27.6 22.4	21.4 15.6	11.8 5.9	8.3 2.9	6.7 1.2
Peanuts - Georgia PRZM-EXAMS Tifton Loamy Sand	2 ground spray, pre/post -plant 40-	2	15.4 14.6	11.5 9.7	6 3.4	3.6 1.4	2.7 0.51
Cotton - Miss. (PRZM-EXAMS)	day interval 6 aerial, foliar	1	14 11.2	10.8 7.8	5.7 2.8	3.7 1.3	3 0.55
loring Silt Loam Tobacco - NC (PRZM-EXAMS) Norfolk Loamy Sand	spray appl. 1 pre-plant, ground spray	5	40.6 39.6	31 27	2.8 14.7 8.6	7.7 3.1	5.4 1.0

C.1.3.3 TCP Groundwater Metabolite Exposure

SCI-GROW is an empirical model based upon curve fitting observations from prospective groundwater studies to parameters apparently assumed important. Even the developer states in the model documentation, "Since the SCI-GROW concentrations are only likely to be approached in a very small percentage of drinking water sources which constitute highly vulnerable aquifers, it is not appropriate to use SCI-GROW concentrations for national or regional exposure estimates." With such a disclaimer for parent materials, the utility of using such a model for estimating metabolite concentrations resulting from the metabolism of parent material is in violation of the assumptions on which the model is based (i.e., field observations of parent material in prospective groundwater studies are representative of conservative estimates for contaminated groundwater). The physically correct way to estimate groundwater concentrations for metabolites is to use the parent/daughter relationship many environmental fate models (such as PRZM) have built in. In this way, the proper competition between metabolite formation, dissipation, and transport can be accounted for.

There are many sensitive parameters that are important for characterizing leaching behavior (Cryer and Havens, in press) than those represented by SCI-GROW. However, in lieu of mechanistic-probabilistic approaches for estimating metabolite concentrations in ground water, an estimate for TCP maximum concentrations found in soil can be obtained through knowledge of kinetic formation and degradation. It is erroneous to assume that all of chlorpyrifos will

instantaneously metabolize into 100% of TCP (degradation product of chlorpyrifos). Since SCI-GROW is based upon parent material applied at the soil surface, any modeling for metabolites using SCI-GROW will be based upon 100% instantaneous metabolism.

The known kinetic pathway for TCP can be expressed as

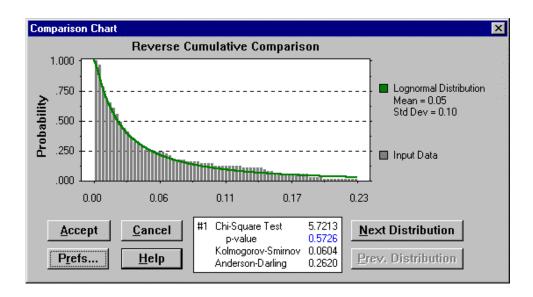
$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$
. where

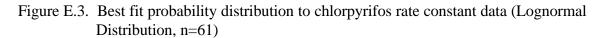
A = mass of chlorpyrifos

R = mass of TCP

S = degradation products of TCP.

The constants k_1 and k_2 are the degradation rate constants for chlorpyrifos and TCP, respectively. Racke (1993) summarized chlorpyrifos (and metabolite) degradation half-lives under laboratory conditions. Termiticide application rates are excluded from this analysis. Half-lives are converted to rate constants (assuming first-order degradation). Probability distributions are then fit to the data using Crystal Ball (Decisioneering, Inc.). The choice for distribution type are lognormal, weibull, gamma, exponential, pareto, extreme value, beta, logistic, normal, triangle, and uniform. A lognormal and exponential distribution provided the best fit for the chlorpyrifos and TCP rate constant data respectively (Figures E.3-E.4).





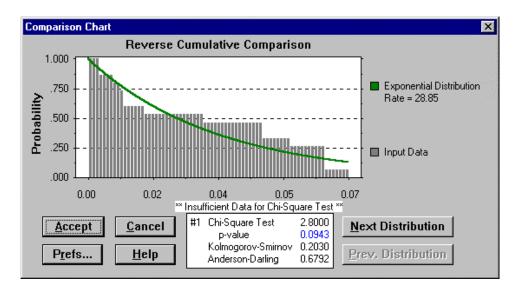


Figure E.4. Best fit probability distribution to TCP rate constant data (Exponential Distribution, n=15)

The solution of the resulting linear ordinary differential equations describing the consecutive reaction metabolic pathway describing TCP formation/degradation can be found in most elementary text in reaction kinetics (Holland and Anthony, 1979) and are provided below. Figure E.5 is a characteristic plot for chlorpyrifos degradation and TCP formation/degradation using average values of $k_1 = 5.513 \times 10^{-2} \, day^{-1}$, and $k_2 = 3.235 \times 10^{-2} \, day^{-1}$. TCP is seen to pass through a relative maximum as it is being simultaneously formed by the metabolism of chlorpyrifos and degraded in soil. In these equations, A and R have been previously defined, and

A_o = initial mass (concentration) of chlorpyrifos.

$$\frac{A}{A_o} = e^{-k_1 t} \tag{1}$$

$$\frac{R}{A_o} = \frac{k_1}{k_2 - k_1} \{ e^{-k_1 t} - e^{-k_2 t} \}$$
 (2)

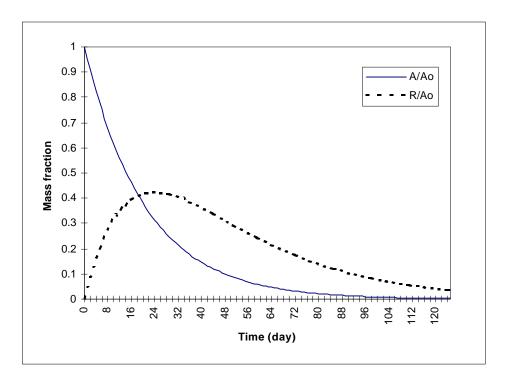
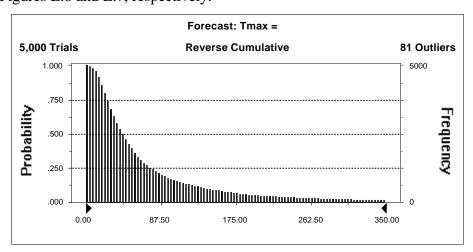


Figure E.5. Characteristic representation for chlorpyrifos degradation and TCP formation/degradation in soil (average values used for rate constants)

The occurrence (and magnitude) for the relative maximum for TCP from Eq. 2 (and seen by the dashed line in Figure E.5) can be found by setting the first derivative to zero and solving for the time of occurrence. Substituting this time back into Eq. 2 gives the magnitude for the maximum mass of TCP in soil. Using the distribution of rate constant data as given by Figures E.3-E.4, the time of maximum mass (Tmax) and the magnitude for the maximum TCP predicted in soil (R/A_o) is given by Figures E.6 and E.7, respectively.



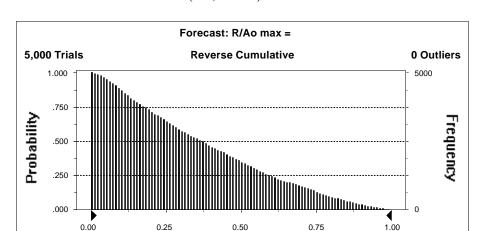


Figure E.6. Reverse cumulative probability distribution for the time (days) until the maximum amount of TCP is observed (i.e., Tmax)

Figure E.7. Reverse Cumulative Distribution for the maximum fraction of TCP observed in soil (given as a fraction of applied chlorpyrifos).

Clearly, assuming that 100% of chlorpyfos is metabolized to 100% of TCP instantaneously has a probability of occurrence of 0.0%. The distribution in Figure E.7 has an average of R/A_o=0.40, indicating the maximum TCP mass (i.e., R) seen from the metabolism of chlorpyrifos is 40% of the applied mass of chlorpyrifos. If one focuses on the worst case value of 10% exceedence, then the maximum amount of TCP seen in soil is ~79%. This is still even higher than that reported on lab and field observations of 44% (Kennard, 1996) and between 16.5 - 77% of applied (Racke et al., 1990). Thus, SCI-GROW predicted groundwater concentrations for TCP are unjustifiably high since 100% of the chlorpyrifos application is not instantaneously converted to 100% TCP (as would have to be the case to avoid contradicting the assumptions/data observations that SCI-GROW is based¹).

¹ SCI-GROW is a regression model which uses parent material that is 100% available on the day of application for leaching, runoff, degradation, etc. Metabolites do not initially exist once a pesticide application is made, but form in soil/soil-pore water following an application. Thus, to use SCI-GROW for metabolite groundwater concentrations violates the data characteristics from which the model is generated.

C.2 GENEEC Simulations and Techniques Used to Refine PRZM-EXAMS Simulations

The 10th percentile half-life value for chlorpyrifos aquatic dissipation (via lab and field observations) is 7.08 days. GENEEC and PRZM-EXAMS simulations assumed the aerobic aquatic half-life for chlorpyrifos was infinite. GENEEC was therefore rerun using the corrected value for aerobic aquatic dissipation. All other physicochemical values and chlorpyrifos use rates used by EFED scientists are held fixed. The values listed as Dow AgroSciences and Dow AgroSciences-aerobic aquatic are the Dow AgroSciences GENEEC runs using the EFED values (Dow AgroSciences) and the refined aerobic aquatic half-life value of 7.08 days (Dow AgroSciences-aerobic aquatic), while the column EFED represents the values tabulated by EPA in the draft EFED document. The "Dow AgroSciences-aerobic aquatic" values are reported (as bold) in Table E.2 in the main document.

Corn - foliar spra	y (GENE	EEC)	1 ground spray,	
			unincorporated	
Time avg. [day]	EFED	DAS	DAS-aerobic aquatic	
0	5.5	5.51	5.38	
4	4.8	4.77	4.16	
21	2.7	2.60	1.52	
60		1.50	0.60	

Corn - foliar spray (GENEEC)			1 aerial appl
Time avg.	EFED	DAS	DAS-aerobic
[day]			aquatic
0	7.7	7.64	6.96
4	6.8	6.74	5.56
21	3.8	3.6	2.02
60	2.3	2.03	0.79
	Time avg. [day] 0 4 21	Time avg. EFED [day] 0 7.7 4 6.8 21 3.8	Time avg. [day] EFED DAS 0 7.7 7.64 4 6.8 6.74 21 3.8 3.6

1 2			3 aerial appl. 14-day interval
Time avg.	EFED	DAS	DAS-aerobic
[day]			aquatic
0	24	23.29	18.03
4	21.5	20.58	14.24
21	11.7	10.84	5.15
60	6.8	5.99	2.03

Corn - granular, pre-plant (GENEEC) 1 ground appl., incorporated 4"

Time avg.	EFED	DAS	DAS-aerobic	
[day]			aquatic	
0	1.66	1.7	1.66	
4	1.44	1.4	1.27	
21	0.81	0.8	0.46	
60	0.51	0.5	0.18	

Corn - granula	ar, post-plant,		1 ground appl. 7" T		
(GENEEC)		Band, 1" incorp.			
Time avg.	EFED	DAS	DAS-aerobic		
[day]			aquatic		
0	8.63	8.63	8.63		
4	7.48	7.42	6.6		
21	4.2	4.06	2.41		
60	2.6	2.37	0.95		

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Corn - granular, foliar, (GENEEC) 2 aerial appl. 14-day interval

Time avg.	EFED	DAS	DAS-aerobic
[day]			aquatic
0	6.35	6.35	6.35
4	5.5	5.46	4.86
21	3.1	2.99	1.77
60	1.9	1.74	0.7

Replication of the EFED PRZM-EXAMS simulation runs could not be made since details as to the actual modeling input parameters used were not provided or summarized anywhere within the draft EFED document. Therefore, a procedure to estimate what refined EECs would be when corrected for an aerobic aquatic half-life of 7.08 days had to be generated. The approach used is based upon the GENEEC model. GENEEC is run for each of the PRZM-EXAMS scenarios listed on pages 25-26, first using EFED input properties (aerobic aquatic half-life = infinity), followed by using a corrected aerobic aquatic half-life of 7.08 days. The scaled difference between each GENEEC simulation (at each time average interval) is used to correct the PRZM-EXAMS predicted EEC tabulated on pages 25-26. In addition, a 90-day average EEC correction had to be obtained since GENEEC only extrapolates out to 56 days. It is found that the scaled difference at each time average interval can be approximated by an exponential function. Thus, a corrected 90-day average PRZM-EXAMS EEC can be obtained. A sample calculation is provided below.

The first two columns summarize the EFED PRZM-EXAMS predictions given on pages 25-26. The third and fourth columns represent results from GENEEC simulations using EFED physicochemical properties and corrected for the aerobic aquatic dissipation rate, respectively. The fifth column is the fraction reduction given by column 4 divided by column 3. This fraction reduction is then multiplied by the original PRZM-EXAMS predicted EEC to arrive at an estimated value when an aerobic aquatic half-life of 7.08 days is used.

A plot of fraction reduction vs. time average is given in Figure A.1, with the exponential fit¹ to the data. Coefficients in this exponential function are obtained by linear regression. This exponential function is then used to estimate the fraction reduction at 90 days, which is then used to correct the 90-day average PRZM-EXAMS value. The last column is simply the original PRZM-EXAMS predicted EEC corrected by the fraction reduction column.

Time avg. [day]	PRZM- EXAMS, Corn IA	GENEEC - DAS EFED properties	GENEEC - DAS with corrected aerobic aquatic value	fraction reduction	PRZM/EXAMs Estimate
0	4	1.57	1.45	0.923567	3.69
4	3.1	1.38	1.15	0.833333	2.58
21	1.6	0.74	0.42	0.567568	0.91
60	1	0.42	0.16	0.380952	0.38
90	0.7			0.188741	0.13

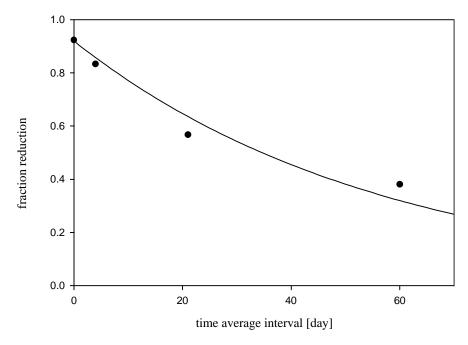


Figure A.1. Example of exponential curve fit to fraction reduction between GENEEC simulations with and without aerobic aquatic metabolism (t 1/2 = infinity or 7.08 days)

¹ Fraction reduction = $a \exp\{-b*[time average]\}$, where a and b are coefficients obtained by the linear regression.

Results of this analysis for all scenarios represented in the table on pages 25-26 are summarized below.

Site		Applicati	on Appl. Rate	e			
		Method	(lbs ai/A)	<u> </u>			
Corn - Iowa (PRZM-EXAN	MS) 1 ground	spray 3				
Marshal	l Silty Clay L	oam appl., inc	orp. 2"				
	Corn-IA	GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Marshall	EFED prop	DAS-aero	Estimate	reduction		
	s-c-l						
0	11.1	6.09	5.82	10.61	0.955665	0.96	1.88E-02
4	8.7	5.31	4.55	7.45	0.856874		
21	4.5	2.87	1.66	2.60	0.578397		
60	2.7	1.64	0.6	0.99	0.365854		
90	1.9			0.33	0.17615		

Site		Application Method	on Appl. Rate (lbs ai/A)	=			
Corn - GA sp	pray (PRZM-EX	KAMS) 11 aerial,	foliar 1	_			
Cowarts San	dy Loam	appl.					
	EFED EEC	GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Corn GA	EFED prop	DAS-aero	Estimate	reduction		
0	15.8	56.52	42.53	11.89	0.752477	0.75	1.75E-02
4	12.8	49.93	32.63	8.36	0.653515		
21	7.4	26.3	11.82	3.33	0.44943		
60	5.6	14.53	4.65	1.79	0.320028		

0.67

0.155956

Site	Application Method	Appl. Rate (lbs ai/A)
Corn - granular, pre-plant, Iowa (PRZM-EXAMS - Corn Cluster)	1 typical ground appl., incorporated 4"	1.3

90

4.3

	PRZM/Ex	GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Corn IA	EFED prop	DAS-aero	Estimate	reduction		
0	4	1.57	1.45	3.69	0.923567	0.92	1.76E-02
4	3.1	1.38	1.15	2.58	0.833333		
21	1.6	0.74	0.42	0.91	0.567568		
60	1	0.42	0.16	0.38	0.380952		
90	0.7			0.13	0.188741		

Site	Application Method	Appl. Rate (lbs ai/A)
Corn - granular, pre-plant, Miss.	1 typical ground	1.3
(PRZM-EXAMS - Corn Cluster)	appl., incorporated	
	4"	

	PRZM/Ex	GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Corn MS	EFED prop	DAS-aero	Estimate	reduction		
0	4.6	1.57	1.45	4.25	0.923567	0.92	1.76E-02
4	3.7	1.38	1.15	3.08	0.833333		
21	1.9	0.74	0.42	1.08	0.567568		
60	1.1	0.42	0.16	0.42	0.380952		
90	0.7			0.13	0.188741		

Site		Application Method	on Appl. Rate (lbs ai/A)				
Citrus - Florio	la (PRZM-E	XAMS) 2 airblast	appl., 3.5	_			
Adamsville Sa	and	30-day in	terval				
		GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Citris	EFED prop	DAS-aero	Estimate	reduction		
0	27.6	36.08	29.34	22.44	0.813193	0.81	1.65E-02
4	21.4	31.88	23.27	15.62	0.729925		
21	11.8	16.79	8.39	5.90	0.499702		
60	8.3	9.28	3.29	2.94	0.354526		
90	6.7			1.23	0.183632		

Site	Application Method	Appl. Rate (lbs ai/A)
Peanuts - Georgia PRZM-EXAMS	2 ground spray,	2
Tifton Loamy Sand	pre/post -plant 40-	
	day interval	

		GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Peanuts	EFED prop	DAS-aero	Estimate	reduction		
0	15.4	13.96	13.23	14.59	0.947708	0.95	1.79E-02
4	11.5	12.09	10.21	9.71	0.8445		
21	6	6.55	3.72	3.41	0.567939		
60	3.6	3.76	1.47	1.41	0.390957		
90	2.7			0.51	0.189533		

		Method	(lbs ai/A)	_			
Cotton - Miss	. (PRZM-EXAN	MS) 6 aerial, fol	liar 1	_			
loring Silt Lo	am	spray appl.					
		GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Cotton	EFED prop	DAS-aero	Estimate	reduction		
0	14	32.28	25.89	11.23	0.802045	0.802	1.65E-02
4	10.8	28.54	20.56	7.78	0.720392		
21	5.7	15.02	7.43	2.82	0.494674		
60	3.7	8.29	2.92	1.30	0.352232		
90	3			0.55	0.18231		
G.,		A 1' ('	4 1 D 4	=			
Site		Applicatior Method	Appl. Rate (lbs ai/A)				
Tobacco - NC	(PRZM-EXAM	(IS) 1 pre-plant	, 5	_			
Norfolk Loam	ny Sand	ground spra	ıy				

Appl. Rate

Application

		GENEEC - DAS	GENEEC - DAS	PRZM/EXAMs	fraction	a	b
Time avg.	Tobacco	EFED prop	DAS-aero	Estimate	reduction		
0	40.6	18.38	17.92	39.58	0.974973	0.975	1.79E-02
4	31	15.9	13.86	27.02	0.871698		
21	14.7	8.65	5.05	8.58	0.583815		
60	7.7	4.99	1.99	3.07	0.398798		
90	5.4			1.05	0.193996		

C.3. Surface Water and Groundwater Monitoring

C.3.1 Correction of Errors

Site

C.3.1.1 Exposure Characterization, Ground Water Assessment, p 33

"Chlorpyrifos residues have been detected in drinking water wells in at least 12 states at levels which greatly exceed the 20 ppb lifetime Health Advisory (HA)."

The characterization of contaminated drinking water wells is erroneous for several reasons. First, these events occur at the time of application of termiticide barrier treatments and are related to site-specific characteristics of the treatment location rather than chemical properties. Unknown to the applicator, there is a preferential travel path for the injected emulsion to enter the drinking water well. This is not a chlorpyrifos-specific situation; all barrier termiticide products applied using industry-standard treatment volumes are equally likely to contaminate wells by preferential flow. It is the well that is contaminated, not the groundwater source. After the emulsion dries, the chlorpyrifos is immobilized by sorption to soil particles, greatly reducing the probability of any

significant further transport. Although the frequency of well contamination is low (Thomas and Chambers, 1997, MRID 44235001), Dow AgroSciences recognizes there is the potential for adverse human health effects in a small sub-population of the U.S. and has voluntarily implemented a product stewardship program that minimizes exposure of affected residents to chlorpyrifos residues in drinking water wells. This program is centered on a comprehensive remediation procedure carried out by professional applicators. Immediately upon notification by the homeowner, the applicator advises the homeowner to cease using suspected contaminated water until after remediation and analytical confirmation of water is conducted showing acceptability for consumption (based on the published EPA HAL). Decontamination is initiated by superchlorination of the well water. Simultaneously, an activated charcoal filter is placed on the supply line to the household water tap. Following completion of this procedure, there is no exposure level or duration that is significant relative to any meaningful toxicity threshold value and the well is restored to its previous condition.

It is also appropriate to point out that information contained in Thomas and Chambers (1997, MRID 44235001), which was not mentioned in the draft EFED science chapter, documented that approximately 46% (1993), 62% (1994), 71% (1995) and 76% (1996) of the suspected well incidents analyzed in this report had initial sample results which were non-detectable for chlorpyrifos (LOQ = 1 ppb). One final point that needs to be clarified regarding MRID 44235001 is the normal distance between the structure being treated and the well head which was suspected to be contaminated. Our analysis showed that over 70% of suspected well incidents were within 30 feet of the structure, with the remaining 30% of the suspected well incidents being spread out over the next 70 feet. It is important to realize that the data used to calculate distance to the well head was made up of approximately 60% of the suspected well incidents which were non-detectable for chlorpyrifos on the initial sampling. As such, the "100 foot distance" cited on pages 36 and 38 in the draft EFED science chapter, accounting for 97% of the suspected well incidents analyzed, should be viewed with caution.

"In a well-water monitoring study conducted on a sand soil, chlorpyrifos and its degradates, TCP and 2-methoxy-3,5,6-trichloropyridine (MOTCP), were not detected (detection limits 0.250 ug/L, 50.00 ug/L, and 10.00 ug/L, respectively) at any sampling interval in the water from two wells located in an orange grove in Highlands County, Florida that received three, 1 lb ai/A applications of chlorpyrifos (MRID 40059001)."

The actual reported TCP levels in this study were considerably lower than 50 μ g/L. The non-detect level was set at less than one-half the lowest quantitation level of 0.05 ppm. Examination of the data tables reveals a report of 2 μ g/L gross TCP, and the analyst recently indicated by personal communication that a gross value of 1 μ g/L would have been reported, if observed. The overall average TCP concentration was much lower than 50 μ g/L in this study. Therefore, the assumption that vulnerable groundwater used for drinking water may be contaminated with TCP at a level of up to 50 μ g/L is not supported by these data. The SCI-GROW prediction for TCP is also in error because the parent/daughter transformation kinetics are not accounted for properly. See the modeling section above for appropriate modeling of parent/daughter transformation kinetics and Wolt, 1997 for an example of correct modeling of parent/daughter product leaching using PRZM's transformation kinetics routines.

C.3.1.2 Exposure Characterization, Drinking Water Assessment, p 37

Drinking Water Source	Exposure Duration	Chlorpyrifos	TCP	
Ground water, except where termiticidal applications occur.	acute or chronic	0.1	86	
Ground water, termiticide use areas.	acute or chronic	2000	>20001	

¹ This estimate for TCP in ground water because of the termiticide use is highly uncertain because there are no monitoring data and the screening models cannot be appropriately applied to predict impacts from this type of use.

The footnote states that the screening models cannot be appropriately applied to predict impacts from termiticide use. This statement is true for both the parent molecule, chlorpyrifos, and the degradate, TCP. The EPA SCI-GROW model developer and science chapter author recognizes the data set used to derive SCI-GROW came from agricultural prospective groundwater studies, which cannot predict leaching from a termiticide barrier treatment. More importantly, minimum

roof overhang and final grade requirements in building codes greatly reduce exposure of barrier treatments adjacent to building foundations to rainfall. Without rainfall, there is no driving force for chemical leaching through soil. Therefore, monitoring data for this use pattern is not necessary.

"Acute and chronic concentrations of TCP in flowing waters:

Based on the high mobility and environmental persistence of TCP relative to chlorpyrifos parent, concentrations of TCP in surface waters are likely to be much higher than chlorpyrifos per se. The maximum modeled concentrations are 404 mg L^{-1} (acute, 4-day) and 304 mg L^{-1} (chronic, 60-day) for the sweet corn use, we used these values as the upper limit on our estimates of TCP concentrations in flowing waters."

GENEEC does not account for the kinetics of parent/degradate transformation. Thus, the TCP predictions from GENEEC are erroneous. It is impossible to set an aerobic soil metabolism half-life for chlorpyrifos to 180 days and then have 100% of the parent converted to TCP two days after application during a GENEEC run. Studies of the rise and decline of chlorpyrifos metabolites at agricultural use rates consistently show relatively low amounts of TCP with respect to the mass of applied chlorpyrifos due to mineralization (Appendix C1; Racke, 1993). Therefore, assuming 100% instantaneous conversion at any time after application is unreasonable.

C.3.2 Uncited Studies

The Agency did not cite the following study submitted by DowElanco: Poletika (1995, MRID 43823901), a review of existing chlorpyrifos surface water monitoring studies.

C.3.3 Omissions of Other Relevant Data

C.3.3.1 Exposure Characterization, Analytical Monitoring Studies in Surface Waters, p 28

A key surface water monitoring publication was omitted (Richards and Baker, 1993). This study reports multiple-year data from time-stratified, event-driven sampling that effectively captures both peak and long-term average pesticide concentrations in Midwestern agricultural watersheds vulnerable to runoff. It is generally recognized in the scientific community as the most comprehensive monitoring study conducted to date. Further, significant amounts of chlorpyrifos

are used in these watersheds. The Richards and Baker publication was summarized in MRID 43823901, which was not cited (see above). The study is on-going; more recent chlorpyrifos data was obtained from the authors and analysed in the Dow AgroSciences unpublished report GH-C 4660, submitted November 18, 1998 (Giesy et al., 1998) (also Giesy et al., in press).

C.3.4 Differences in Interpretation

C.3.4.1 Exposure Characterization, Surface Water Fate and Exposure Assessment, p 26

"The above model-based EECs for a pond are in the range of 0.7 to 40 ppb for chlorpyrifos, whereas the available monitoring data for flowing waters are in the ppt range. . . . the computer generated EECs represent screening levels for most surface waters even if they approximate upper bound concentrations that might be seen in actual edge of the field pond."

The EPA author clearly states that the computer-generated EECs represent screening levels for most surface waters. If these EECs produce exceedences of LOCs, then the appropriate procedure is to conduct a more refined exposure estimate that will generate more realistic values. This is the approach endorsed by a multi-stakeholder work group of expert scientists that included EPA representatives (SETAC, 1994.). It is obvious that consistent predictions of chlorpyrifos concentrations in the low to high ppb range are merely screening levels. If they commonly occurred, there would be widespread and repeated fish kills resulting from non-point source contamination of surface water. Such fish kills are not observed.

C.3.4.2 Exposure Characterization, Analytical Monitoring Studies in Surface Waters, p 28

"The monitoring data represent flowing water receiving pesticide loadings from partially cropped, partially treated watersheds much of which is not adjacent to the water body. Therefore, such data may more accurately represent exposure of aquatic organisms to chlorpyrifos in the flowing water of actual watersheds than the computer estimated EECs for a one-acre farm pond."

This is further EPA opinion that computer-estimated EECs for a ten-hectare field draining into a one-hectare pond do not predict actual environmental concentrations relevant to assessing adverse ecological effects.

"Although there is substantial overlap between a number of USGS stations and chlorpyrifos use sites, sampling sites do not necessarily represent watersheds where chlorpyrifos is most heavily used. Therefore they may reflect less exposure to chlorpyrifos than in watersheds where it is heavily used."

Dow AgroSciences unpublished report GH-C 4660, submitted November 18, 1998 (Giesy et al., 1998) (also Giesy et al., in press) presents data demonstrating widespread chlorpyrifos use in monitored watersheds that are vulnerable to runoff. Detailed geographic sales information are combined with computer predictions of generic runoff vulnerability for USGS NAWQA Study Units and other monitoring studies in a comprehensive analysis of this issue.

"Also, chlorpyrifos concentrations in lakes and ponds both adjacent and not adjacent to treated fields may sometimes be substantially greater than in flowing water."

The statement "may sometimes be" is vague. What are the specific data citations?

"In the citrus field study, two water samples collected on Day 1 tested positive for chlorpyrifos. The measured concentrations in these two water samples were 1.2 and 486 ppb, which clearly bracket all the above, modeled EECs."

In the Appendix E4 we show that the water contamination in the citrus field study was due to misapplication. As pointed out in the modeling section above, this type of off-site transport cannot be modeled by the GENEEC/PRZM-EXAMS farm pond scenario. The cited study is not representative of appropriate product use near water bodies, and thus does not report measured concentrations which can be used to validate the modeled EECs. A more realistic interpretation of these measured concentrations is that they confirm the overly conservative nature of GENEEC/PRZM-EXAMS farm pond predictions.

C.3.4.3 Exposure Characterization, Ground Water Assessment, p 33

"The largest detection [of chlorpyrifos] in about 3000 NAWQA wells across the country has been <0.04 ug/L (Table 7). The Pesticides in Ground Water Database has a maximum reported value of 0.65 ug/L. These compare with a SCI-GROW ground-water screening concentration of 0.11 ug/L for the sweet corn use.

"For TCP, in the absence of usable monitoring data, we estimate the most vulnerable ground water usable for drinking water may be contaminated with this compound at a level of about 85.7 ug/L (the SCI-GROW value for the sweet corn use)."

A maximum reported value of $0.65 \mu g/L$ is meaningful only when compared to the entire distribution of values. This is possible with the tabular presentation of NAWQA data, but not for the Pesticides in Groundwater Database (table titled *Chlorpyrifos Residue Distributions in Major Ground-Water Monitoring Studies*, p 35). Also, the maximum value is always suspect in a retrospective groundwater monitoring study. With wells, point source contamination is a possible explanation. The nature of the maximum observation should be specified.

The sweet corn use occurs only when ears are on the stalk. Therefore, very little chlorpyrifos will reach the soil surface under most conditions and be available for leaching. Also, product use in sweet corn is minimal, and it is the only use that allows a large number of repeat applications. When considered together, these points indicate the SCI-GROW prediction is overly conservative.

C.3.4.4 Exposure Characterization, Drinking Water Assessment, p 37

"Based on the existing monitoring database which covers a large part of the U.S., we believe the exposure estimates below are moderately conservative (i.e., exceed actual exposure by a several-fold factor) for a majority of the U.S. population. However, it must be emphasized that estimated exposure levels from these datasets incorporate data from some areas where chlorpyrifos usage is probably very low; residues in surface waters could be much higher in some areas if chlorpyrifos usage is more pervasive in the watershed."

What is the evidence that chlorpyrifos usage is probably very low? A recent analysis in Dow AgroSciences unpublished report GH-C 4660, submitted November 18, 1998 (Giesy et al., 1998) (also Giesy et al., in press) suggests otherwise. Moreover, monitoring studies targeting pesticide analytes typically establish sampling sites where product use is expected.

C.3.4.5 Part 1: Ground Water Exposure Levels (Except Termiticidal Uses)

"No ground-water monitoring data are available for the major chlorpyrifos degradate 3,5,6-trichloro-2-pyridinol (TCP), but modeling based upon existing monitoring data for other pesticides in vulnerable ground water indicates that TCP residues may range up to $86 \text{ mg } L^{-1}$ in shallow ground water used for drinking water. Residues would of course, likely be much lower in less vulnerable ground water."

The cited citrus study (MRID 40059001) had a lowest quantitation limit of 50 μ g/L and reported gross TCP levels down to 2 ppb. The average reported value was considerably lower than 50 μ g/L. Therefore, the 86 μ g/L maximum predicted by the SCI-GROW screening model is overly conservative. Worst-case Tier 2 PRZM modeling conducted for triclopyr/TCP predicted a maximum TCP pore water concentration observed at 100 cm of 0.104 μ g/L (Wolt, 1997). Groundwater concentrations for this simulation would be lower due to dilution in the aquifer.

C.3.4.6 Part 3: Surface Water Exposure Levels - Rivers and Streams

"A further limitation is that these monitoring data do not focus on the types of water bodies where the highest exposure levels are most likely to occur: small lakes and reservoirs."

The trend for highest exposure levels to occur in small lakes and reservoirs is based on data for highly mobile, relatively persistent herbicide products. This trend has not been demonstrated for an insecticide such as chlorpyrifos, which is relatively immobile and relatively non-persistent at agricultural use rates. Where treatments are applied at high rates with the intent of establishing the persistence necessary for long-term protection against termites, surface water contamination is rare and restricted to water bodies very close to the application site. During the 60-day public comment period Dow AgroSciences will submit a report analyzing termiticide surface water contamination incidents that supports the previous statement.

"Chronic concentrations of chlorpyrifos parent in flowing waters:

Our overall conclusion from this analysis by three methods is that the available monitoring data imply that chlorpyrifos chronic concentrations are unlikely to exceed 0.1 mg L^{-1} (the highest 90-day exposure level we confirmed to date was 0.06 mg L^{-1}). However, since it is not clear if the monitoring data cover the most vulnerable watersheds and because modeling indicates exposure at higher levels in more vulnerable streams in higher-use watersheds is at least a plausible hypothesis, we recommend maintaining the upper-bound estimate for chronic exposure to chlorpyrifos in flowing surface waters at $0.4 \text{ mg } L^{-1}$ (see the section entitled "Conclusions on likely Drinking Water Exposure Levels" for further details)."

The third method of analysis and the section entitled "Conclusions on likely Drinking Water Exposure Levels" could not be found in the document. Regardless, we question the relevance of the 0.06 µg/L 68-day, not 90-day, time-averaged concentration. What is the toxicological

endpoint for this time frame of exposure? In the section titled, *Exposure Characterization*, *Water Resource Assessment on p. 21*, EPA states:

"Chlorpyrifos is not currently regulated under the Safe Drinking Water Act (SDWA). Therefore no MCL has been established for it and water supply systems are not required to sample and analyze for it. It has one-day and 10 day HALs of 30 mg/L, and a lifetime HAL of 20 mg/L. The limited data EFED has on chlorpyrifos in surface water as well as summaries from the NAWQA program suggests that it is probably unlikely that the annual average concentrations of chlorpyrifos will exceed the lifetime health advisory or that peak or short term average concentrations will exceed the 1-10 day health advisory in the actual surface water sources for drinking water."

EPA cites only the 1- and 10-day and lifetime HALs as appropriate endpoints in a risk assessment. Therefore, the 68-day average concentration does not apply. Annual average values are necessary for lifetime risk. The following alternative estimate for the 68-day average concentration provides an upper bound for the annual average.

For the White River Study Unit, the maximum reported value from the years of intensive sampling was $0.13~\mu g/L$ (data used for distributional analysis in Dow AgroSciences unpublished report GHC 4660, submitted November 18, 1998 (Giesy et al., 1998) (also Giesy et al., in press)). The ratio of highest 68-day average to maximum reported value is 0.06/0.13 = 0.46. It is plausible that this ratio applies to all 20 of the study units in group one of NAWQA. Therefore, a more reasonable representative chronic exposure value for a 68-day exposure period would be $0.46~x~0.4~\mu g/L = 0.18~\mu g/L$. When the appropriate weighting is applied to concentrations observed for times outside the 68-day period, the annual average would be much lower than $0.18~\mu g/L$.

Appendix D: Terrestrial Exposure Profile

D.1 Modeling

The use of the Kenaga/Fletcher residue levels is most strongly justified in the case where no compound-specific data is available. The Agency attempts to justify their use of the most conservative residue numbers by comparison of the Kenaga/Fletcher values to the highest values

D.1.1 Non-Granular Exposures and Assumptions — Differences in Interpretation

cited by Racke (1993) and concludes there is agreement "in most cases" between the field and

nomogram values; the lower residue levels are essentially ignored.

Risk assessors are cautioned by Pfleeger et al. (1996), of the U.S. EPA Environmental Research Laboratory (Corvalis, Oregon) about the use of the Kenaga nomogram for predicting maximum plant residues:

Assessors of pesticide risks need to be made aware that numbers from the nomogram do not reflect the large variance in plant residues and that the nomogram should not be used when immediate postapplication data are available.

This variablity is to be expected due to variable canopy cover if nothing else; in one case a factor of five to 10 difference in residues were seen between the upper and the lower height samples in a mature cornfield (Kamble et al. 1992).

Neither Hoerger and Kenaga nor Fletcher et al. give the maximum residue values for insects that are listed in the document. The use of 135 ppm and 45 ppm for small insects are inventions of the EFED of EPA; they appear nowhere in the peer review literature. No data have been provided by EPA or others to support the use of those values for insects. Likewise, the use of 15 ppm and 7 ppm for large insects appear nowhere in the peer-review literature. Again, no data have been provided by EPA to support the use of those values.

Kenaga suggested the residues on large insects and small insects could be estimated by use of plant categories. Kenaga grouped small insects with forage crops giving 58 ppm and 33 ppm as

maximum and mean residue values. Large insects were grouped with seeds and fruits and given a maximum value of 10 - 12 ppm. No data supporting these values have ever been presented. Insects are never mentioned in Fletcher et al. It is only prudent to recognize the prediction of insect residues based upon residues measured in plants are likely to be inaccurate. Quoting again from Pfleeger et al.:

Kenaga also suggested that these concepts could be applied to estimating the residues on insects. Although the concepts may be valid, to our knowledge no validation of this approach has been undertaken. While the present nomogram may be used for making such estimates (Urban and Cook 1986), considerable reflection should be exercised prior to using the nomogram or a revised nomogram for estimating pesticide residues on anything other than plants.

D.1.2 Omissions

For multiple applications, the Agency employs the "Fate Model" to estimate wildlife dietary foodstuff residues. This model is totally undocumented and, as far as we are aware, unavailable to registrants. The description of the modeling runs, supposedly in Appendix III of the document, consists only of a title page. The lack of documentation and unavailability of the model are both in direct conflict with the Agency's own guidance on the performance and documentation of modeling studies as communicated by EFED personnel to the ACPA FIFRA Modeling Working Group in 1995. Registrants, including Dow AgroSciences, have made a good faith effort to follow this guidance in their submission of modeling studies. Without documentation, it is difficult, if not impossible, to make any evaluation of the applicability or quality of the Agency's modeling results found in this document.

The document points out the decreasing probability of an organism encountering maximum residue levels when there are multiple applications. It would be more appropriate to use the actual field-measured residue values, within a probabilistic framework (using the 90th percentile field residue values, for example). Such residue data have been submitted by Dow AgroSciences in large field studies, some of which are cited in summary form in the document (e.g., Gallagher et al., 1994; McQuillen et al., 1998a, McQuillen et al., 1998b).

The science chapter states on page 16:

"Measured residue levels reported in field studies on corn, citrus and golf courses sprayed with chlorpyrifos support the use of maximum residue levels for risk assessment."

Analysis of Dow AgroSciences field monitoring studies, performed under GLP, do not support this conclusion. For Tier I risk assessment purposes, it is appropriate to employ the maximum monitored residue values. However, for a more refined assessment, the use of a probabilistic approach is warranted. The table below summarizes the field data which has been submitted and includes the monitored range and 90th percentile of the foodstuff residues.

Summary of field residue data for wildlife foodstuffs (all concentrations in ppm, normalized to 1 lb a.i./acre).

Matrix	Kenaga-	monitored	mean	90 th	notes and reference
	Fletcher residue (max/typical)	range	residue	percentile	
short grass	240/85	50-233	124	193	Turfgrass
					Booth, 1989
seeds	15/7	4-5	4.5	n/a	Treated chicken scratch
					Booth, 1989
seeds	15/7	0.06- 0.25	0.22	n/a	Treated seed heads
					McQuillen et al., 1998a (alfalfa)
seeds	15/7	0.08 - 0.095	0.08	n/a	Treated seed heads
					McQuillen et al., 1998b (citrus)
forage	135/45	15-363	134	269	corn foliage
					Frey et al., 1994
forage	135/45	<0.2 - 115	10.4	19.3	adjacent foliage
					Frey et al., 1994
forage	135/4	8-76	27	50	citrus foliage
					Gallagher et al., 1994
forage	135/45	0.1-86	9	24.7	treated non-crop foliage
					Gallagher et al., 1994
invertebrates	135/45 (small)	<0.3-7.7	2.7	n/a	on-field invertebrates
	15/7 (large)				Frey, et al, 1994
invertebrates	135/45 (small)	0.1-9.3	2.0	7.8	on-field invertebrates
	15/7 (large)				Gallagher et al., 1994
invertebrates	135/45 (small)	0.04-6	1.8	n/a	on-field invertebrates
	15/7 (large)				McQuillen et al., 1998a (alfalfa)

n/a = insufficient data

Another assumption employed in the document is a seven-day foliar half-life, based on an analysis of the data in Racke (1993). This is overly conservative, based on an evaluation of the field residue submitted for several major cropping situations. In corn, Frey et al. (1994) measured the

decline of chlorpyrifos residues in corn foliage and non-target plants after repeated sprays of Lorsban 4E Insecticide. Based on average data values, the half-life of the residues was observed to be about 2.2 - 2.5 days in both plant types. In citrus fields, McQuillen et al. (1998b) found the residues in seed heads to decline with a half-life of about 5.5 days; while Gallagher et al. (1994) found residues in both crop and non-crop plants to decline even more quickly, with an average half-life of about 3.5 days. Taking the three studies together, the foliar half-life, normalized to 1 lb a.i./A, is about 2.7 days (r^2 =0.8).

D.2 Granular Exposures and Assumptions

D.2.1 General Comment

Dow AgroSciences objects to the use of the undocumented and speculative LD₅₀/ft² criterion to assess granular exposure. The use of LD₅₀/ft² quotient is based on an internal EPA memorandum (Felthousen, 1977). The intent of the index was to provide a standardized method to classify granular pesticides. Felthousen stated "I realize there are pertinent points which I have either understated or simply overlooked, and as such, this document should not be construed as being a definitive statement on the subject. Instead, I would prefer to think of this paper as a framework from which more comprehensive, and as such, a more reliable classification scheme could be developed." Felthousen stated that "support for this approach can be found in the literature." He cites Dewitt (1966) "Losses of birds may be expected if the quantity of toxicant per square foot equals or exceeds the quantity causing deaths of quail in short term feeding tests." What DeWitt actually said is "These data do not establish a basis for relating dietary concentrations (ppm) causing mortality to qualities applied for control of pests. However they indicate a possible relationship between the lethal quantity (mg/bird), as determined short-term feeding tests (emphasis added), and the quantity of toxicant per unit area. For the three compounds studied, it appears (emphasis added) that losses of birds may be expected if the quantity of toxicant per square foot equals or exceeds quantities causing death of quail in short term feeding tests (emphasis added)." Felthousen also states that "additional support" (for the use of pesticide per unit area) is provided by Tucker who reported that "field kills have happened in many instances

when the amount of toxicant per acre have exceeded 50,000 mallard LD50's (assuming 1 kg mallard body weight). This misleading paraphrase was apparently from Tucker and Crabtree (1969). What these authors actually said is "On the basis of field mortality data, these results suggest that when the amount **sprayed** (emphasis added) per acre exceeds 50,000 to 100,000 times the LD50 for 1-kg mallards, it is probable that some bird mortality will result." It is apparent this approach has a weak basis in science and it is clear that over the past 22 years the EPA has conducted no research supporting the continued use of LD_{50}/ft^2 criterion. Indeed, the work of Best and his colleagues clearly indicates that avian exposure to granular pesticides is much more complex than the simple assumption that LD_{50}/ft^2 represents a measure of risk to terrestrial species.

D.2.2 Errors

The document goes into great detail on pages 18-19 regarding bird preference for corncob granules as a grit or mistaken food source. However, chlorpyrifos formulated for agricultural use (Lorsban 15G granular insecticide) employs only clay granules, so the arguments presented about preference for corncob granules are irrelevant. It is also not clear how the results of the granule-preference argument are incorporated into the risk assessment.

On page 21 of the document, the formulae for computing risk quotients for banded treatments are incorrect. The formulas do not yield dimensionless quantities. Corrected formulae are as follows:

Granular band/T-band, unincorporated

$$RQ = \frac{(oz \ a \ i. \ / \ 1000 \ ft \ row) \ x \ (28,340 \ mg \ / \ oz) \ x \ 1 \ ft^2 \ for aging \ area}{1000 \ ft \ row \ x \ band \ wi \ dt \ h \ (ft) \ x \ LD50 \ (mg \ ai \ / \ kg \ bw) \ x \ kg \ bw}$$

Granular band/T-band, incorporated

 $RQ = \frac{(oz\ a\ i.\ /\ 1000\ ft\ row)\ x\ (28,340\ mg\ /\ oz)\ x\ fraction\ at\ surface\ x\ 1\ ft^2\ foraging\ area}{1000\ ft\ row\ x\ band\ wi\ dt\ h\ (ft)\ x\ LD50\ (mg\ ai\ /\ kg\ bw)\ x\ kg\ bw}$

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These formulae assume that birds will be present <u>only</u> on the application bands. This is unlikely, based on bird behavioral studies (discussed in detail in Kendall et al., 1998). A simple refinement of this approach would be to incorporate the proportion of the field area made up by the application bands. This value would depend upon the band spacing and widths, but would be roughly 25% for normal practices. Thus, the equations would become:

Granular band/T-band, unincorporated

```
RQ = \frac{0.25 \text{ fraction as bands x (oz a i. / 1000 ft row) x (28,340 mg / oz)}}{1000 \text{ ft row x band width (ft) x LD50 (mg ai / kg bw) x kg bw}} \times \frac{16 \text{ ft}^2 \text{ for aging area}}{1000 \text{ ft row x band width (ft) x LD50 (mg ai / kg bw) x kg bw}}
```

Granular band/T-band, incorporated

```
RQ = \frac{0.25 \, fraction \, as \, bands \, x (oz \, a \, i. \, / \, 1000 \, ft \, row) \, x (28,340 \, mg \, / \, oz) \, x \, fraction \, at \, surface \, x \, 1 \, ft^{\, 2} \, for aging \, area}{1000 \, ft \, row \, x \, band \, wi \, dt \, h (ft) \, x \, LD50 (mg \, ai \, / \, kg \, bw) \, x \, kg \, bw}
```

The formula for in-furrow treatment makes similar assumptions and the formula is in error. The corrected formula is:

$$RQ = \frac{(oz \ a \ i. \ / \ 1000 \ ft \ row) \ x \ (28,340 \ mg \ / \ oz) \ x \ 0.01 \ exp \ osed \ x \ 1 \ ft^2 \ for \ agi \ ng \ area}{1000 \ ft \ row \ x \ row \ wi \ dt \ h(ft) \ x \ LD50 \ (mg \ ai \ / \ kg \ bw) \ x \ kg \ bw}$$

A refinement, as described above for banded treatments, could be made to consider the fraction of the field area made up by the treated rows.

D.2.3 Omisssion

The document makes the following statements (p 18):

"Granules may also be consumed by wildlife which feed on earthworms, slugs or other soft-bodied soil organisms to which the granules may adhere."

and (p 20)

"For example, if a 70 to 80-gram bird consumed eight earthworms with an average of 6 to 10 granules attached to or inside each earthworm, the exposure would be equivalent to the house sparrow LD_{50} value."

No data are presented, and Dow Agrosciences is unaware of any data to support the contention that granules sticking to soft bodied invertebrates are consumed by animals incidental to the consumption of the invertebrates. In fact, Frey et al. (1994), found no statistical difference in the chlorpyrifos residues in invertebrates from liquid- and granular-treated plots and all the residues found were below the level of analytical quantitation.

D.2.4 Uncited Studies

EFED assumes a degree of incorporation of granules in various application scenarios, based upon U.S. EPA (1982). Within a low-tier assessment framework, these values are reasonable; however, more recent data has been collected by a number of researchers (Erbach and Tollefson, 1983; Hummel et al., 1992; Idema et al., 1993; Fischer and Best, 1995; and Tollner and Cryer, 1997). Collectively, they characterized granule placement with a variety of corn planters and active ingredients (including Lorsban 15G granular insecticide) using band, T-band, and in-furrow application methods with/without further incorporation. The results are presented in Table XXX. Table XL summarizes the data from Table XXX according to method of application and the presence or absence of an incorporation device included as part of the corn planter. Table XXX can be used directly as model input if the intent is to express incorporation efficiency as a distribution of values, or Table XL can be used as a source of single point estimate of incorporation efficiency.

Table XXX. Percentage of granules remaining on soil surface after application of granular rootworm insecticide to corn by a variety of planters and application methods

	Type of		Method of		% of Applied	
Formulation	Planter ^{1,3}	Placement ²	Incorporation	Tillage ³	on Surface	Reference
Furadan 10G	JD M-E	T-Band	Press Wheel	CT	31.0	Hummel et al., 1992
Furadan 10G	JD M-E	T-Band	Press Wheel	CT	23.8	Hummel et al., 1992
Furadan 10G	JD M-E	T-Band	Press Wheel	CT	18.1	Hummel et al., 1992
Fur 10G/Lors 15G	JD M71/JD M7000	T-Band	Press Wheel	CT	14.7	Erbach & Tollefson, 1983
Aztec 2G	?	T-Band	Press Wheel	CT	11.3	Idema et al., 1993
Silica Granule	?	Band/T-Band	Press Wheel	CT	10.2	Fischer & Best, 1995
Silica Granule	?	Band/T-Band	Press Wheel	CT	8.8	Fischer & Best, 1995
Silica Granule	?	Band/T-Band	Press Wheel	CT	7.4	Fischer & Best, 1995
Silica Granule	?	Band/T-Band	Press Wheel	CT	7.1	Fischer & Best, 1995
Silica Granule	?	Band/T-Band	Press Wheel	CT	6.2	Fischer & Best, 1995
Lorsban 15G	JD M-E	T-Band	Press Wheel	CT	6	Tollner & Cryer, 1997
Aztec 2G	?	T-Band	Press Wheel		5.4	Idema et al., 1993
Silica Granule	?	Band/T-Band	Press Wheel	CT	4.6	Fischer & Best, 1995

Aztec 2G	?	T-Band	Press Wheel		4.3	Idema et al., 1993
Silica Granule	?	Band/T-Band	Press Wheel	CT	4.2	Fischer & Best, 1995
Lorsban 15G	JD M-E	T-Band	Press Wheel	CT	4	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	NT	4	Tollner & Cryer, 1997
Aztec 2G	?	T-Band	Press Wheel		3.8	Idema et al., 1993
Silica Granule	?	Band/T-Band	Press Wheel	CT	3.3	Fischer & Best, 1995

Table XXX. Percentage of granules remaining on soil surface after application of granular rootworm insecticide to corn by a variety of planters and application methods (con't)

	Type of		Method of		% of Applied	
Formulation	Planter ^{1,3}	Placement ²	Incorporation	Tillage ³	on Surface	Reference
Lorsban 15G	JD M-E	T-Band	Press Wheel	?	3	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	MT		Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	?	2 2	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	?	1.7	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	?	1.6	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	NT	1	Tollner & Cryer, 1997
Lorsban 15G	JD M-E	T-Band	Press Wheel	MT	<u>0</u>	Tollner & Cryer, 1997
				Mean	7.3	-
				Median	4.5	
Fur 10G/Lors 15G	JD M71/JD M7000	T-Band	Drag Chain	CT	7.9	Erbach & Tollefson, 1983
Furadan 10G	JD M-E	T-Band	Tines	CT	6.8	Hummel et al., 1992
Fur 10G/Lors 15G	JD M71/JD M7000	T-Band	Tines	CT	5.8	Erbach & Tollefson, 1983
Furadan 10G	JD M-E	T-Band	Tines	CT	4.9	Hummel et al., 1992
Furadan 10G	JD M-E	T-Band	Tines	CT		Hummel et al., 1992
Turuum 100	VB 1.1 E	1 24114	111100	Mean	3.7 5.8	11411111101 00 411, 1992
				With	2.0	
Fur 10G/Lors 15G	JD M71/JD M7000	BandR	Drag Chain	CT	16.0	Erbach & Tollefson, 1983
Fur 10G/Lors 15G	JD M71/JD M7000 JD M71/JD M7000	BandR	Tines	CT	7.4	Erbach & Tollefson, 1983
Tur 100/Lors 130	3D W1/1/3D W1/000	Danuk	Times	Mean	11.7	Libacii & Tolicisoli, 1703
Fur 10G/Lors 15G	JD M71/JD M7000	BandR	Press Wheel	CT	40.2	Erbach & Tollefson, 1983
Furadan 10G	JD M71-F	In-Furrow	Press Wheel	CT	0.8	Hummel et al., 1992
Furadan 10G	JD M71-F	In-Furrow	Press Wheel	CT	0.4	Hummel et al., 1992
Furadan 10G	JD M71-F	In-Furrow	Press Wheel	CT	0.5	Hummel et al., 1992
				Mean	0.57	

¹ **JD M-E** = John Deere Max-Emerge; **JD M71, M71-F** = John Deere Model 71 Flexi-planter; **JD M7000** = John Deere Model 7000

³ CT = Conventional Tillage; MT = Minimum Tillage; NT = No Tillage; ? = Not stated

Table XL. Percentage of corn rootworm formulation granules remaining on the soil surface after application by a variety of methods. Data are summarized from Table 2.

	% of Applie		
Method of Application	Mean ¹	Median	Number of Values
Band/T-Band + press wheel	7.3±7.3	4.4	26
T-Band + press wheel + tines/chains	5.8±1.6		5
In-furrow + press wheel	0.57±0.2		3

² For purposes of this table the following definitions are used. **T-Band** = granules applied with a bander centered over the open seed furrow and producing a band of granules about 6 inches wide in front of a press wheel that followed. **In-furrow** = granules applied into open seed furrow in front of a press wheel, with no bander in place. **Band** = band application in front of press wheel. **BandR** = band application behind press wheel.

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Band behind press wheel	40.2	 1
Band behind press wheel + tines/chains	11.7±6.1	 2

¹Plus/minus values are the standard deviation of the mean.

The data of Erbach & Tollefson (1983), employing a banded treatment <u>behind</u> a press wheel, is especially interesting in that only 40.2% of the material remained on the surface in contrast to the EPA assumption of 100% availability for an unincorporated band treatment. For T-banded applications, the 90th percentile percent at the surface value is approximately 9.2%.

Appendix E: Aquatic Effects Profile

E.1 Laboratory Toxicity Studies

E.1.1 Uncited Studies/Differences in Interpretation of Evidence

E.1.1.1 Aquatic Toxicity Assessment - (EFED p 63)

E.1.1.1.1 Study selection criteria/Use of SMAV

The selection of aquatic toxicity studies to support effect concentrations used by the EFED in risk quotient calculations would appear to be driven only by the lowest-available endpoint concentration for any standard test species, regardless of the quality or technical merit of the chosen study. This practice is at odds with good scientific principals and with U.S. EPA policy as outlined in the water quality criteria for the Great Lakes system (U.S. EPA 1995d):

"For each species for which at least one acute value is available, the species mean acute value (SMAV) shall be calculated as the geometric mean of the results of all acceptable flow-through acute toxicity tests in which the concentrations of test material were measured with the most sensitive tested life stage of the species. For a species for which no such result is available, the SMAV shall be calculated as the geometric mean of all acceptable acute toxicity test with the most sensitive tested life stage.....Geometric means, rather than arithmetic means are used here because the distributions of sensitivities of individual organisms in toxicity tests on most materials the distributions of sensitivities of species within a genus are more likely to be log-normal than normal."

For those organisms having more than one study examining the toxicity of chlorpyrifos, the EFED selection of available aquatic toxicity data for chlorpyrifos should be based on an SMAV algorithm, such as that outlined above. If we apply this U.S. EPA algorithm to the EFED aquatic toxicity database on chlorpyrifos, we find, for example, that EFED used a 96-h LC₅₀ value (range) for the bluegill sunfish (*Lepomis macrochirus*) of 1.8-2.4 μg/L. However, these data are based on a static exposure, nominal concentration exposure experiment (Mayer and Ellersick, 1986) rather than a 96-h LC₅₀ value of 10 μg/L based on flow-through, measured dosing concentrations

(Phipps and Holcombe, 1985). Similarly, the chronic toxicity study with *Daphnia magna* cited by EFED (McCann 1979) did <u>not</u> report measured dose levels and should be replaced with a static-renewal study by Adema and DeRuiter (1990) that did report measured solution concentrations of chlorpyrifos.

In summary, the absence of a study characterization algorithm in the EFED document is a serious shortfall and requires standardization of a study selection algorithm prioritized on flow-through exposures and measured concentrations and the use of an SMAV for all acceptable toxicity endpoint values for a given species. As noted in sections E.1.1.1.2 to E.1.1.1.4 below, Dow AgroSciences has examined the available acute and chronic scientific literature on chlorpyrifos and have proposed new toxicity effect concentrations based on use of the SMAV for standard test species.

Another area of misinterpretation by the EFED authors involved the issue of exposure duration in acute toxicity studies. The potential impact of any chemical compound on an organism involves the concentration of the compound <u>and</u> the duration of exposure; this latter variable is particularly important for aquatic organisms, some of whom have life spans measured in weeks or months. At greater concentrations of toxicant, shorter times of exposure are required to generate a specific response and, vice versa; this time-toxicity concentration issue is commonly a reciprocal relationship. In standardized laboratory toxicity tests, organisms are exposed to constant concentrations of toxicant for specified periods of time, typically 48 and 96 hours for invertebrate and vertebrate acute testing, respectively. In order to appropriately compare the results of any acute toxicity study with another, the period of exposure must be the same or a mathematical treatment of the data may be necessary prior to any comparison or averaging. The EFED authors have erred in this respect, as in their examination of freshwater invertebrate toxicity of chlorpyrifos (pp 70-71) they have compared directly acute toxicity endpoints of different exposure durations. The EFED data table (p 71) on freshwater invertebrate toxicity lists two LC₅₀ values for the stonefly (Gammarus lacustris) as 0.11 and 0.76 ppb (a.i.), but fails to note that the values represent 96- and 24-hr exposure periods, respectively. As such, the values cannot be directly

compared or used collectively to calculate a standard SMAV for *Gammarus lacustris*. In fact, the EFED acute freshwater invertebrate toxicity datatable on chlorpyrifos (pp 70-71) does not mention the length of any exposure period for any species. Neither do any of the presented EFED acute data tables on estuarine fish or estuarine invertebrates. Clearly, EFED must standardize the exposure period for all supporting aquatic toxicity studies as it is not scientifically credible to compare effect concentrations for a given species that were conducted with different exposure timeframes. In environmental toxicology, exposure periods of 48 and 96 hours are the generally accepted standards for invertebrate and vertebrate acute testing, respectively. An exception to this rule is the testing of the standard marine invertebrates (i.e., the mysid shrimp, *Mysidopsis bahia*, or eastern oyster, *Crassostrea virginica*), which require a 96-hour exposure period.

E.1.1.1.2 Acute Toxicity Studies

The attached data tables on vertebrate (Appendix Table E(1)) and invertebrate (Appendix Table E(2)) acute toxicity experiments predominately include studies conducted with the standard vertebrate and invertebrate exposure periods of 96 and 48 hours, respectively; a considerable number of the studies cited in Appendix Tables E(1) and E(2) were not included in the EFED document, either as core or supplemental data. All available LC₅₀ values for a given species and constant exposure timeframe were used to calculate SMAVs for each sensitive species; the SMAVs were calculated using a geometric mean technique (U.S. EPA 1995d). The SMAV from sensitive test species with standard exposure timeframes should be used as the "toxicity concentrations" (see Appendix Table E(4)) in the calculation of freshwater acute risk quotient (RQ) values.

E.1.1.1.3 Chronic Toxicity Studies

With regard to chronic effect concentrations of chlorpyrifos to freshwater and saltwater invertebrates, the EFED document did <u>not</u> include several potentially important studies; the uncited reports and their respective NOEC/LOEC values are presented in Appendix Table E(3). Two of the reports involved the water flea or daphnid (*Daphnia magna*) and one with the mosquito (*Wyeomia smithii*). As noted in Appendix Table E(3), the freshwater invertebrate

chronic toxicity study with *Daphnia magna* cited by EFED (McCann, 1979, MRID 41073401) did <u>not</u> report measured dose levels of chlorpyrifos and yet was noted as fulfilling core U.S. EPA data requirements (EFED p 72). However, an uncited chronic daphnid study noted in Appendix Table E(3) by Adema and DeRuiter (1990) did report measured solution concentrations of chlorpyrifos. In this report, the authors observed an NOEC of $0.056 \,\mu\text{g/L}$ and an LOEC of $0.10 \,\mu\text{g/L}$, slightly higher values than those reported by McCann (1979). The NOEC values from three chronic daphnid studies have been averaged into a mean NOEC value of $0.061 \,\mu\text{g/L}$.

A saltwater chronic mean NOEC of $0.003 \,\mu\text{g/L}$ has been calculated from the data of U.S. EPA (1986) and Sved et al. (1993). While neither of these studies qualifies as having both measured dose levels and verifiable NOEC values, a mean chronic NOEC value is presented for saltwater invertebrates in Appendix Table E(3), $0.003 \,\mu\text{g/L}$.

E.1.1.1.4 Revised Acute and Chronic Toxicity Effect Concentrations

The data compiled in Appendix Tables E(1)-E(3) present a more complete listing of the available acute and chronic aquatic toxicity studies on chlorpyrifos. The studies selected for EFED were simply by the lowest effect concentration for a given toxic impact, rather than application of an SMAV algorithm, as endorsed by a U.S. EPA water quality criteria document (U.S. EPA 1995d). If we instead decide to use all acceptable toxicity data for calculation of an SMAV a given species and employ standard exposure durations, it is possible to generate "revised" acute and chronic toxicity effect concentrations to replace those used by the EFED in their calculation of aquatic RQ values on chlorpyrifos. These revised concentrations are presented in Appendix Table E(4) for standard freshwater and saltwater organisms. The revised effect concentrations were selected from Appendix Tables E(1)-E(3) as the mean toxicity concentration (SMAV or NOEC) for standard freshwater and saltwater organisms with a exposure duration of either 48 or 96 hours for invertebrate or vertebrate test species, respectively. An exception to this policy was the use of a 96-hour exposure period for the estuarine invertebrate acute toxicity test with the mysid, *Mysidopsis bahia* (see Appendix Table E(2)).

To summarize, the freshwater fish acute LC₅₀ (96-hr) effect level represents the geometric SMAV for bluegill sunfish (3.4 μ g/L), while the freshwater fish reproduction NOEC remains unchanged from the EFED value of 0.57 μ g/L for fathead minnows. The revised freshwater invertebrate acute LC₅₀ (48-hr) value is the SMAV of 0.55 μ g/L for the daphnia (*Daphnia magna*) compared to the EFED value of 0.10 μ g/L that was based on a single *Daphnia magna* acute study (see Appendix Table E(2)). The revised chronic freshwater invertebrate NOEC of 0.061 μ g/L represents the mean NOEC from three *Daphnia magna* life-cycle studies (Appendix Table E(3)), while the saltwater invertebrate NOEC is calculated to be 0.003 μ g/L. The new saltwater fish acute LC₅₀ (96-hr) effect level is based on the SMAV for the Atlantic silverside (*Menidia menidia*), with a value of 1.3 μ g/L, while the saltwater fish reproduction NOEC remains unchanged from the EFED concentration of 0.28 μ g/L. The revised saltwater invertebrate LC₅₀ (96-hr) is based on the SMAV for the mysid (*Mysidopsis bahia*), with a value of 0.043 μ g/L.

Appendix Table E(1): Analysis of Species-Mean Acute Values (SMAVs) for freshwater and saltwater vertebrates. Data summarized by Barron and Woodburn (1995).

							Species Mean Acute Value		
			C44				(SMAV) ²		Cited in
Organism	Taxonomic Name	Age	Study Design	Test Subst.	Time (d)	Endpoint	(SMAV) (ng/mL or ug/L; ppb)	Reference	EFED (Y/N)?
Freshwater		9-			(-/		(9= +: -9, pp)		
Bluegill	Lepomis macrochirus	0.5-0.8g	F/S,N/M	T(97%)	4	LC50	3.4	Mayer and Ellersieck 1986; Johnson and Finley	M&E only
Longnose killifish	Fundulus similis	N/A	F, N	T(92%)	4	LC50	4.1	Schimmel et al. 1983	N
Stickelback	Pungitius pungitius	Α	F,N	T(>99%)	4	LC50	4.7	van Wijngaarden et al.	N
Rainbow trout	Oncorhynchus mykiss	N/A	N/A	N/A	4	LC50	8	Lembright and Cope 1965; Mayer and Ellersieck	Y
Ide	Leuciscus idus	N/A	S-R,N	T	4	LC50	10	Douglas and Bell	N
Cutthroat trout	Oncorhynchus clarki	0.9-1.4g	S,N	T(97%)	4	LC50	14	Mayer and Ellersieck 1986; Johnson and Finley	Y
Lake trout	Salvelinus namaycush	N/A	S,N to F,N	T(97%)	4	LC50	150	Mayer and Ellersieck 1986	Y
Fathead minnow	Pimephales promelas	0.1g	F,M	T(>99%)	4	LC50	194	Holcombe et al. 1982; Jarvinen and Tanner 1982; Phipps and Holcombe	Y
Roach	Rutilus rutilus	N/A	S-R,N	T í	4	LC50	250	Douglas and Bell	N
Mosquitofish	Gambusia affinis	N/A	S,N	N/A	4	LC50	280	Carter and Graves 1973	N
Tilapia	Tilapia mossambica	6-10g	S,N	T(95%)	4	LC50	420	Subburaju and Selvarajan 1988; Karim et al. 1985; Dutt and Guha	N
Channel catfish	Ictalurus punctatus	0.8-7.9g	S,N to F,M	T(97%)	4	LC50	475	Phipps and Holcombe 1985; Johnson and Finley	N
European eel	Anguiila anguilla	20-30g	S,N	T(97%)	4	LC50	540	Ferrando et al. 1991	N
Goldfish	Carrassius auratus	10.7g	F,M	N/A	4	LC50	806	Phipps and Holcombe	N
Saltwater	_								
Striped bass	Morone saxatilis	0.06 - 4.8g	F,N	T(>99%)	4	LC50	0.58	Korn and Earnest	Y
Tidewater silverside	Menidia peninsulae	<1-60 d	F,M	T(92%)	4	LC50	0.75	Clark et al. 1985; Mayer	Y
California grunion	Leuresthes tenuis	<1-28 d	F,M	T(92%)	4	LC50	1.0	Borthwick et al. 1985	Y
Atlantic silverside	Menidia menidia	<1-53 d	F,M	T(92%)	4	LC50	1.3	Mayer 1987; Borthwick et al. 1985; Schimmel et al.	Υ
Gulf killifish	Fundulus grandis	J	F,M	T(92%)	4	LC50	1.8	Mayer 1987	Y
Longnose killifish	Fundulus similis	J	F,M	T(92%)	4	LC50	4.1	Mayer 1987; Schimmel et al.	Y
Mummichog	Fundulus heteroclitus	N/A	F,N	T(>99%)	4	LC50	4.7	Thirugnanam and Forgash	N
Topsmelt	Altherinops affinis	7-28 d	S,N	T(92%)	4	LC50	5.0	Hemmer et al. 1992	N
Striped mullet	Mugil cephalus	J	F,M	T(92%)	4	LC50	5.4	Schimmel et al. 1983	Υ
Inland silverside	Menidia beryllina	72-d	F,M	Т	4	LC50	4.2	Clark et al. 1985; Hemmer et al.	Υ

^{*}S, static; S-R, static renewal; F, flow-through; M, measured concentration; N, nominal ² Geometric mean of all acceptable 96-hr LC50 values for a given

Appendix Table E(2): Analysis of Species-Mean Acute Values (SMAVs) for freshwater and saltwater invertebrates. Data summarized by Barron and Woodburn (1995); Burgess (1988) taken from EFED document.

Species Mean

Organism	Taxonomic Name	Age	Study Design*	Test Subst.	Time (d)	Endpoint	(SMAV) ^z (ng/mL or ug/L; ppb)	Reference	Cited in EFED (Y/N)?
Freshwater									` '
Mosquito	Culex pipiens	4th instar	S,N	EC	2	LC50	0.20	Rettich 1979	N
Cladoceran	Daphnia pulex	N/A	F.M	EC	2	LC50	0.21	van Wijngaarden and Leeuwangh 1989	N
Amphipod	Gammarus pseudolimnaeus	N/A	F,M	N/A	2	LC50	0.30	Siefert 1984; USEPA 1986	N
Mayfly	Emphemerella sp.	N/A	F,M	N/A	2	LC50	0.40	Siefert 1984	N
Cladoceran	Daphnia magna	N/A to <1d	N/A to S,M	N/A to Tech.	2	LC50	0.55	Kersting and van Wijngaarden 1992; McCarty, 1977; Burgess 1988	Υ
Mosquito	Aedes cantans	4th instar	S,N	EC	2	LC50	0.90	Rettich 1979	N
Caddisfly	Laptoceride sp	N/A	S,M	CR	2	LC50	0.90	Siefert 1984	N
Backswimmer	Plea Sp.	N/A	S,M	N/A	2	LC50	2.40	Siefert 1984	N
Stonefly	Claassenin sp.	N	S,N	T	3	LC50	20.0	Day and Scott 1990	N
Amphipod	Gammarus pulex	N/A	F,N	EC	4	LC50	0.07	van Wijngaarden et al. 1993	N
Cladoceran	Ceriodaphnia dubia	<1-d	S,M	T(99%)	4	LC50	0.08	CDFG 1993	N
Amphipod	Gammarus lacustris	Α	S,N	T(97%)	4	LC50	0.11	Sanders 1972	Y
Mysid	Neomysis mercedis	<1-d	S,M	T(99%)	4	LC50	0.14	CDFG 1993	N
Amphipod	Gammarus pseudolimnaeus	N/A	F,M	N/A	4	LC50	0.20	Siefert 1984	N
Mayfly	Cloen dipterum	N	F,N	EC	4	LC50	0.30	van Wijngaarden et al. 1993	N
Cladoceran	Daphnia longispina	Α	S-R,N	EC	4	LC50	0.30	van Wijngaarden et al. 1993	N
Amphipod	Gammarus fasciatus	N/A	S,N	Т	4	LC50	0.32	Sanders 1972	N
Stonefly	Pteronarcella badia	N	S,N	T	4	LC50	0.38	Sanders and Cope 1968	N
Cladoceran	Simocephalus vetulus	J	S-R,N	EC	4	LC50	0.50	van Wijngaarden et al. 1993	N
Stonefly	Claassenia sabulosa	N	S,N	Т	4	LC50	0.57	Sanders and Cope 1968	N
Water strider	Gerris gibbifer	Α	F,N	EC	4	LC50	2.0	van Wijngaarden et al. 1993	N
Isopod	Asellus aquaticus	Α	S-R,N	T(>99%)	4	EC50	2.7	van Wijngaarden et al. 1993	N
Mayfly	Caenis horaria	N	F,N	EC	4	LC10	3.0	van Wijngaarden et al. 1993	N
Crayfish	Orconectes immunis	1.8g	F,M	N/A	4	LC50	6.0	Phipps and Holcombe 1985	N
Diptera	Chaoborus obscuripes	L	F,N	EC	4	LC50	6.6	van Wijngaarden et al. 1993	N
Stonefly	Pteronarcys californica	N	S,N	Т	4	LC50	10.0	Sanders and Cope 1968	N
Isopod	Proasellus coxalis	Α	F,N	EC	4	EC50	20.0	van Wijngaarden et al. 1993	N
Crayfish	Procambarus clarki	15-30 g	S,N	N/A to T(>99%)	4	LC50	29.3	Cebrian et al. 1992, Chang and Lange 1967	N
Saltwater		_							
Brown shrimp	Penaeus aztecus	J	F,N	T(92%)	2	EC50	0.20	Mayer 1987	Y
Grass shrimp	Palaemonetes pugio		F,N	T	2	LC50	1.5	Mayer 1987	Y
Pink shrimp	Penaeus duorarum	J	F,N	T(92%)	2	EC50	2.4	Mayer 1987	Υ
Blue crab	Callinectes sapidus	J	F,N	T(92%)	2	EC50	5.2	Mayer 1987	Y
Mysid	Mysidopsis bahia	1-d	S,N to F,M	T(92%)	4	LC50	0.043	Schimmel et al. 1983; Mayer 1987; Borthwick and Walsh 1981	Y
Korean shrimp	Palaemon macrodactylus	N/A	S,N	T(99%)	4	LC50	0.25	Earnest 1970	N
Grass shrimp	Palaemonetes pugio	Α	S-R,N	Т	4	LC50	0.40	Key and Fulton 1993	N
Grass shrimp	Palaemonetes pugio	î	F.N	Ť	25	LC50	0.29	Key and Fulton 1993	N N
Orass sillillp	r alacinoricios pugio	L	1 ,14	'	25	L030	0.25	Ney and I diton 1330	IN

^{*}S, static; S-R, static renewal; F, flow-through; M, measured concentration; N, nominal concentration

Appendix Table E(3): Chronic toxicity of chlorpyrifos to freshwater and saltwater invertebrates. Data summarized by Barron and Woodburn (1995); McCann (1979) taken from EFED document.

							Mean ^t			
			Exposure			NOEC	NOEC	LOEC ^q		Cited in
Organism	Taxonomic Name	Age	Period (d)	Test Subst.	Method*	(ug/L)	(ug/L)	(ug/L)	Reference	EFED (Y/N)?
Freshwater										
Daphnid	Daphnia magna	<1 d	LC (21)	Technical	S-R, M	0.056		0.10	Adema and DeRuiter 1990	N
Daphnid	Daphnia magna	<1 d	LC (21)	Technical	S-R, N	0.10		0.30	Kersting and van Wijagaarden 1992	N
Daphnid	Daphnia magna	N/A	N/A	Technical	N/A, N	0.04	0.061	0.08	McCann 1979 (from EFED)	Υ
Mosquito	Wyeomia smithii	2nd instar	7	Technical	S, N	N/A		1.00	Strickman 1985	N
Saltwater										
Mysid	Mysidopsis bahia	N/A	LC (21)	Technical	N/A	0.002		0.004	USEPA 1986	N
Mysid	Mysidopsis bahia	<1 d	LC (35)	Technical	F, M	0.0046	0.003	0.010	Sved et al. 1993	Υ

^{*}S, static; S-R, static renewal; F, flow-through; M, measured concentration; N, nominal concentration

² Geometric mean of all published equal exposure LC50 values for a given species

^z NOEC: No-observed effect concentration

^t Geometric mean of available NOEC values

^q LOEC: Lowest-observed effect concentration

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Appendix Table E(4) Revised acute and chronic toxicity effect concentrations for freshwater and saltwater organisms.

Test Description	Toxicity Effect Concentration (µg/L or ppb)
Freshwater Fish Acute LC ₅₀	3.4
Freshwater Fish Reproduction NOEC	0.57
Freshwater Invertebrate Acute LC ₅₀	0.55
Freshwater Invertebrate Reproduction NOEC	0.061
Estuarine Fish Acute LC ₅₀	1.3
Estuarine Fish Reproduction NOEC	0.28
Estuarine Invertebrate Acute LC ₅₀	0.043
Estuarine Invertebrate Reproduction NOEC	0.003

E.2. Aquatic Field Studies/Biomonitoring

E.2.1 Uncited Studies/Differences in Interpretation of Evidence

E.2.1.1 Freshwater Microcosm Toxicity/Simulated Freshwater Field Toxicity (pp 73-83)

In the EFED review of freshwater microcosm/mesocosm/field studies on chlorpyrifos (pp 73-83), the reviewers have overlooked a substantial amount of information on the fate and effects of the compound in these complex aquatic systems. The EFED microcosm/mesocosm review generally focused on studies conducted at the University of California-Riverside (Hurlbert et al., 1970, 1972), the Duluth laboratory of the U.S. EPA (Siefert et al., 1989), and the Dow AgroSciences experiments (Giddings, 1993a, 1993b). The EFED authors overlooked an extensive series of detailed experiments conducted at the Winand Staring Centre in the Netherlands that examined the responses of pond ecosystems to chlorpyrifos exposure (Brock et al., 1993; Crum and Brock, 1994; Cuppen et al., 1995; Leeuwangh, 1994; Leeuwangh et al., 1995; Van Wijngaarden et al., 1996). The following is a summation of both the previously-presented microcosm/mesocosm studies in EFED, as well as brief summaries of the extensive Dutch experiments. This summary will help to demonstrate that ecosystem functional endpoints are considerably more robust than the simple structural properties of aquatic ecosystems. The results obtained from microcosm/mesocosm studies reveal that changes in community structure can occur without affecting overall community

metabolism, as functional redundancy becomes important, i.e., non-susceptible organisms take over the function of organisms directly or indirectly affected by chlorpyrifos.

Microcosm/mesocosm data are of considerable value to an in-depth risk assessment since these systems are better able to replicate the interactions in dynamic ecological communities. Natural ecosystems show large-scale variations in population and distribution depending on the season, light conditions, water temperature, and nutrient and prey availability. Laboratory studies lack any opportunities for the sort of organism recolonization available in natural ecosystems. Phytoplankton and macrophytes in natural settings present high contact surface areas for pesticide absorption and uptake, thereby reducing the available pesticide for the aqueous phase. Dissolved and particulate organic matter in the water column also present sites for sorption or chelation of hydrophobic organic compounds in natural systems, thereby significantly reducing the amount of chemical available for uptake from the aqueous phase (Day, 1991; Ortego and Benson, 1992) and from sediment (Servos and Muir, 1989).

Consequently, risk evaluations of pesticides using aquatic microcosms/mesocosms would allow evaluation of the effects of environmental perturbation under more realistic conditions than normally exist in laboratory studies. Rather than examine only the response of single species under artificial conditions, microcosm experiments allow ecological responses and their significance to be assessed within the context of a functioning aquatic community. Microcosms and mesocosms are also better suited for determination of the toxicological impact of pulsed doses of chemicals, which by nature are short-lived in the aquatic environment (e.g., use of chlorpyrifos).

E.2.1.1.1 Pond studies at the University of California, Riverside

Experimental ponds at the University of Riverside pond facilities were sprayed four times at two-week intervals with chlorpyrifos (Dursban) at rates of 0.01, 0.05, 0.1 and 1 lb a.i./A (Hurlbert et al., 1970). Chlorpyrifos concentrations measured in the water 4 hours after application were $200 \,\mu\text{g/L}$ at the greatest application rate and $10 \,\mu\text{g/L}$ at the second application rate; if the same

relationship applied to the other rates, the lowest application rate corresponded to approximately 2 μg/L chlorpyrifos. Populations of the dominant zooplankton species, *Cyclops vernalis* (a copepod) and *Moina micrura* (a cladoceran), were reduced by the chlorpyrifos treatments, as was that of corixid *Corisella*. Populations of the copepod *Diaptomus pallidus* and the rotifer *Asplanchna brightwelli* increased in the ponds where *C. vernalis* and *M. micrura* populations were reduced (except for *D. pallidus* at the greatest application rate). Survival and reproduction of mosquitofish (*Gambusia affinis*) were unaffected at the two lowest dose levels, 0.01 and 0.05 lb/A.

To investigate the ecological relationships that led to increases in numbers of *D. pallidus* and *A. brightwelli*, the study was repeated using chlorpyrifos concentrations of approximately 72 and 7.2 μg/L, respectively, repeated three times at two-week intervals (Hurlbert et al., 1972). The responses of *C. vernalis*, *M. micrura*, *D. pallidus*, and *A. brightwelli* were the same as in the first experiment. *C. vernalis* and *M. micrura* recovered in 1 - 3 weeks at the lesser application rate, and in 3 - 6 weeks at the greater rate. Besides *D. pallidus* and *A. brightwelli*, populations of herbivorous rotifers increased soon after *C. vernalis* and *M. micrura* decreased. An algal bloom developed which was attributed to the loss of herbivorous crustaceans; six weeks after treatment, algal densities in ponds at the lesser application rate were twice as great as controls, and those at the greater application rate were 16 times as great as those of the controls. Among the insects, populations of the predaceous taxa (notonectids and corixids) declined after chlorpyrifos treatment and recovered slowly, while the herbivorous insects were less affected and recovered more quickly.

E.2.1.1.2 Littoral enclosure studies at the Duluth EPA laboratory

In a study conducted at the EPA mesocosm facility, littoral enclosures in a pond were sprayed once with chlorpyrifos at rates of ~ 0.003 , 0.03, and 0.1 lb a.i./A (initial chlorpyrifos concentrations of 0.5, 5, and $20 \,\mu g/L$). Populations of the ostracod *Cyclocypris* and all five cladoceran species present in the enclosures were significantly reduced at all application levels four days after treatment with chlorpyrifos (Siefert et al., 1989; Brazner and Kline, 1990).

Copepod densities were less on average in the treated enclosures than in the controls, but few of the differences were statistically significant. Populations of a few rotifer species were reduced at the least application rate, but most were unaffected at the greater application rates, and some were more abundant in the treated enclosures, on average, than in the controls. Populations of most species of chironomids (the dominant insect group) were significantly reduced at all treatment levels four days after treatment with chlorpyrifos. Populations of chironomids recovered to pretreatment levels within 16 days at the lowest treatment level, but were still less than those in the control enclosures after 32 days in the two higher treatment levels. Populations of other insects and the amphipod Hyalella azteca were also affected, while snails, planaria, and protozoa were unaffected or increased in the treated enclosures. An algal bloom occurred in the treated enclosures eight days after chlorpyrifos application. Survival of juvenile fathead minnows (*Pimephales promelas*) exposed in cages in the enclosures was unaffected by any of the chlorpyrifos treatments, while survival of bluegill sunfish (Lepomis macrochirus) was less in the intermediate and highest treatment concentrations. The difference in response of the two fish species was consistent with their observed sensitivity in laboratory studies (Barron and Woodburn, 1995).

Fathead minnow larvae that hatched in the enclosures one week before treatment grew more slowly than those in the control enclosures (Brazner and Kline, 1990). The number and diversity of food items in the stomachs of these fish were less than in the control enclosures at all treatment regimen. The reduction in stomach contents was attributed to a reduction in abundance of invertebrate prey in the enclosures (Brazner and Kline, 1990). The reduced larval growth rate was interpreted as an indirect effect of the chlorpyrifos treatment. However, analysis of food selectivity indicated that fathead minnow larvae in the enclosures (including controls and all enclosures before treatment) preferred rotifers and protozoans to cladocerans and copepods. Rotifers and protozoans were generally unaffected by chlorpyrifos treatment, casting some doubt on the hypothesis that fish growth reduction was caused by reduced food availability. Thus, it is likely that other factors may have been partly or completely responsible.

E.2.1.1.3 Pond microcosm studies by Springborn Laboratories for Dow AgroSciences

These studies were conducted in large outdoor pond microcosms near Lawrence, Kansas (Giddings, 1993a, 1993b). Chlorpyrifos was applied as a surface spray, a slurry of clay particles, or a combination of the two. Dose levels ranged from 0.03 - $3 \mu g/L$, with a single replicate mesocosm at $10 \mu g/L$. As initial chlorpyrifos concentrations in the sprayed microcosms averaged 89% of the nominal values, all references will be to the nominal dose concentrations.

A single spray application of 0.3 μg/L reduced the abundance of cladocerans, copepod nauplii (but not adult *Diaptomus pallidus*), mayflies, and chironomid midges. These effects were temporary, as copepod and cladoceran population densities returned to control levels within two weeks, midges within four weeks, and mayflies within eight weeks. The abundance of rotifers increased. Body weight and survival of juvenile bluegill sunfish were affected at concentrations of 3 and 10 μg/L, but not at 1 μg/L or below. At treatment regimens greater than 1 μg/L, effects were more widespread and more pronounced and recovery took longer. Most rotifer species and some midges (tribe Tanytarsini) were not reduced at any treatment level. Bluegill sunfish growth (length) and total biomass were affected at 1 μg/L and survival was reduced at 3 μg/L (nominal).

Chlorpyrifos applied to the microcosms as three biweekly clay slurry treatments produced similar results. Copepod nauplii (not adult *Diaptomus pallidus*) were the most sensitive, with brief reductions in their populations at exposures as little as $0.03 \,\mu g/L$; cladocerans; ostracods, and some midges were affected at $0.3 \,\mu g/L$. Other midges, as well as mayflies, were reduced by a concentration of $3 \,\mu g/L$. Bluegill sunfish growth (weight, length, and biomass) was reduced at $1 \, ng/L$, and survival was significantly effected at $3 \,\mu g/L$. Most rotifer species and several groups of midges were unaffected at any treatment level. As in the study with spray treatments, most effects at the lesser treatment levels were transient. Copepod nauplii were an exception; at $0.3 \,\mu g/L$ and $1 \,\mu g/L$, nauplii densities were reduced through the end of the season. However, this effect was not completely dose-related as copepod nauplii densities at $3 \,\mu g/L$ were not statistically different (p ≤ 0.05) from control levels seven days following the second slurry application and were

unchanged by the third slurry dosing of chlorpyrifos.

E.2.1.1.4 Microcosm and mesocosm studies in the Netherlands

Researchers at the Winand Staring Centre at Wageningen, the Netherlands, investigated the fate and effects of chlorpyrifos in an extensive series of experiments. Most of the experiments were conducted in 600-L indoor microcosms, while others took place in shallow ditch mesocosms simulating one of the most characteristic aquatic habitats of that country. The results of all studies were fairly consistent and together they present a richly detailed picture of the responses of pond ecosystems to chlorpyrifos exposure.

Most of the studies with indoor microcosms involved single spray applications of chlorpyrifos emulsifiable concentrate formulation at initial chlorpyrifos concentrations of 35 μg/L. Results of the most comprehensive of these experiments were summarized by Cuppen et al. (1995). Chlorpyrifos exposure resulted in direct toxicity to cladocerans, copepods, amphipods, isopods, and insects. The reduction in herbivores resulted in greater growth of periphyton and phytoplankton. As the chlorpyrifos concentration declined, the populations of many herbivores, including copepods, rotifers, snails, and oligochaetes, increased — in response to the increased food supply and decreased competition from other, more sensitive herbivores. The reduction in invertebrate shredders (amphipods and isopods) resulted in decreased rates of litter decomposition.

Ecological responses to 35 μ g/L chlorpyrifos have little relevance to exposures resulting from agricultural applications. However, the Dutch researchers evaluated the effects of lesser chlorpyrifos concentrations in two ways: first, by observing the recovery of populations within the microcosms, and second, by incubating organisms in cages in the microcosms at various times (Leeuwangh et al., 1994). It was found that copepods and some cladoceran populations recovered when chlorpyrifos concentrations decreased to 0.2 μ g/L; populations of other cladocerans recovered when chlorpyrifos concentrations decreased to less than 0.1 μ g/L. Taxa with no source for colonization because they had no resistant life stages, no refugia within the

system, and no access for recolonization from outside, such as insects, amphipods, and isopods, did not recover. However, the potential for these populations to become reestablished was evaluated based on the results of the caged exposures. In this way, the no-effect concentration (NOEC) for *Chaoborus obscuripes* (midge), *Cloeon dipterum* (odonate), and *Gammarus pulex* (amphipod) were determined to be $0.2~\mu g/L$, and that of *Asellus aquaticus* (isopod) was estimated to be $1.3~\mu g/L$.

Effects of low chlorpyrifos concentrations were determined more directly in an experiment with the ditch mesocosms (van Wijngaarden et al., 1996; van den Brink et al., 1996). The mesocosms were sprayed once with chlorpyrifos at initial concentrations of 0.1, 0.9, 6, and 44 μ g/L. The EC10, EC50, and no-effect concentrations for individual taxa were calculated based on the initial 48-hour mean concentrations in mesocosm water. *C. obscuripes, C. dipterum*, and *G. pulex* and *A. aquaticus* were exposed in cages in the microcosm experiment described above. For most arthropod species, the EC50 values ranged from 300 - 600 ng/L. Overall, "a no-observed-effect concentration of 0.1 μ g/L could be derived both at the species and the community level" (van den Brink et al., 1996).

Most taxa affected by greater concentrations of chlorpyrifos in ditch mesocosms recovered before the end of the 24-week study. Crustacea (except *Gammarus pulex*) recovered rapidly even at the greatest treatment level, due to rapid reproduction rates and the presence of resistant resting stages. The amphipod *Gammarus pulex* did not recover, because there was no source for recolonization. This result was "an artifact due to the isolated position of the mesocosms noting that recolonization sources normally exist in natural ecosystems (van den Brink et al., 1996).

In contrast to the indoor microcosm experiments, few indirect effects on non-arthropods were observed in the mesocosm studies. The authors attributed this to the greater complexity of the mesocosms than the microcosms. "A structurally more diverse and complex ecosystem includes more redundant populations and ¼ feedback mechanisms, so indirect effects are harder to

detect" (van den Brink et al. 1996).

We may conclude the following from microcosm/mesocosm studies on chlorpyrifos, particularly the extensive Dutch work overlooked by the authors of the EFED document:

Both microcosm and mesocosm studies have demonstrated that exposure to chlorpyrifos concentrations less than $0.100~\mu g/L$ affect few, if any, aquatic taxa. At concentrations above $0.200~\mu g/L$, effects on invertebrates are more widespread, but nearly all taxa recover within 2 - 8 weeks. At a concentration of $0.500~\mu g/L$ and greater, survival and growth of some fish species may be affected. A concentration of $0.100~\mu g/L$ can be taken as a conservative no-effect concentration for overall ecosystem response and exposures to greater concentrations of chlorpyrifos result in a variety of direct and indirect ecological effects. Crustaceans (notably cladocerans, copepods, ostracods, and amphipods) and some emergent insects (mayflies) were typically the most sensitive taxa, while other insects, rotifers, and snails were typically more tolerant. Almost invariably, some tolerant taxa increase in abundance when their more sensitive competitors are reduced. Populations of affected species generally recover rapidly as chlorpyrifos disappears from the water. The sources for population recovery vary among taxa, but include resistant resting stages, internal refugia, and external ecosystems.

Finally, in their data table summarizing observed fish mortality from aquatic field studies, the EFED authors fail to note the affect of water depth on exposure concentrations of chlorpyrifos (EFED p 72); the data table simply lists the observed fish mortality associated with chlorpyrifos application rates, expressed as pounds (a.i.)/acre. Water depth will clearly have a major, controlling impact on the resulting chlorpyrifos aquatic residues, so it is inappropriate for EFED to present fish kill data as a simple function of chlorpyrifos direct water application rate. As a majority of these dated studies did not report measured residue concentrations of chlorpyrifos, these data should have a very limited use in the EFED risk assessment as it is not possible to correlate fish species field mortality with chlorpyrifos exposure concentration.

E.2.1.2 Biomonitoring in Surface Waters (EFED p 32)

On page 32 of the EFED document, the authors stated:

"A number of biomonitoring studies have identified chlorpyrifos as a problem in several areas around the country. In some areas chlorpyrifos levels have tested toxic to <u>Ceriodaphnia</u> in rainfall, POTW discharges, storm drain systems, and river segments in agricultural areas. Nationwide pesticide monitoring studies indicate widespread chlorpyrifos residues in fish samples......Bioassay of rainfall samples in Sacramento and San Francisco area show chlorpyrifos residue levels which are toxic to <u>Ceriodaphnia dubia</u>, the invertebrate component of EPA's three species bioassay test."

The EFED document anecdotally details the issue of bioassay studies conducted on surface waters from California with the daphnia, *Ceriodaphnia dubia*, that have purportedly identified chlorpyrifos as contributing to the toxicity of some surface waters (EFED pp 32-33). The section also notes that "organophosphate pesticides" have been identified as contributing to bioassay toxicity in a number of states, yet the EFED document fails to cite scientific references in support; the only citation for the bioassay portion of the EFED document is Foe (1995), but this particular citation is not listed in the reference section of the EFED report (pp 211-213).

It is inappropriate to imply that chlorpyrifos is responsible for the observed bioassay toxicity strictly due to detectable concentrations of the chemical in the positive bioassay water samples. The simple co-occurrence of aqueous-phase chlorpyrifos concentrations and bioassay toxicity may not be directly related for a number of reasons. For example, in natural aquatic systems, dissolved and particulate organic matter in the water column and sediment present sites for sorption or chelation of hydrophobic organic compounds, thereby significantly reducing the amount of dissolved chemicals available for biological uptake (Day, 1991; Ortego and Benson, 1992; Servos and Muir, 1989). Aquatic organic matter has been shown to reduce the acute toxicity of various insecticides by factors of 3 - 20 times (Day, 1991; Ortego and Benson, 1992), and gill transport and subsequent bioconcentration of lipophilic pyrethroid insecticides has similarly been shown to be reduced by factors of 5 - 10 (Ortego and Benson, 1992). The available data indicate the

presence of detectable chlorpyrifos concentrations in natural water does not necessarily translate into bioavailable dose levels capable of adversely impacting sensitive aquatic invertebrates.

The authors of EFED suggest that chlorpyrifos is "the source of toxicity" contributing to the observed bioassay mortality of many of the tested surface water samples in the state of California. However, in a peer-reviewed publication (not cited by EFED) discussing the biological effects of pesticides in the San Francisco estuary, Kuivila and Foe (1995) note in their conclusions that "Bioassay mortality corresponded with the highest diazinon concentrations at both sites, and diazinon does explain a good deal of the observed C. dubia toxicity." In addition, the authors stated that "In all samples collected during this study, concentrations of diazinon always exceeded the National Academy of Sciences and National Academy of Engineering recommended guidelines, whereas the dissolved concentrations of chlorpyrifos were less than the recommended EPA criteria on all dates except for February 12 on the San Joaquin River." It therefore appears from available information in the scientific community that, contrary to the conclusions of the EFED chapter, chlorpyrifos may play only a partial role in the bioassay mortality observed in testing of some surface waters around San Francisco, California.

Finally, a fundamental assumption of the bioassay monitoring program is that such tests as the acute *Ceriodaphnia* assay accurately predict instream biological response. However, the EPA's biomonitoring program (which includes *Ceriodaphnia*) is based on detecting instream effects from direct discharge of effluent (point source) from industrial or municipal sources, not non-point sources entering ambient water, i.e., agricultural use of pesticides. The biomonitoring studies were originally developed to confirm results from the EPA's Complex Effluent Toxicity Testing Program (CETTP); this database cites direct discharge damages to downstream, impacted aquatic communities from municipal treatment plants, refineries, coke plants, chemical manufacturing plants, fertilizer plants, steel mills, and other industrial sources, but none involved organophosphate pesticide contamination. Indeed, we are not aware of any developed correlation between *Ceriodaphnia* bioassay results and instream biological responses for the organophosphates. The CETTP studies have focused on areas where instream biological impacts

were known or suspected, and the correlation between *Ceriodaphnia* bioassay results and instream response is weakest where environmental impacts are less severe or not measurable. If one examines the available literature (Birge et al., 1989; Dickson et al., 1992; Eagleson et al., 1980; U.S. EPA, 1985), the *Ceriodaphnia* bioassays frequently indicated toxicity where no instream impacts were found. This is easy to overlook in the database as ~85% of the selected site locations were impacted and could only produce true positives, not false positives. If you examine all the data in the referenced studies looking at <u>non-impacted</u> downstream sites, the frequency of false positives is 57% (30 of 53 - see attached Text Table 1). This high proportion of false positives simply indicates the importance of following screening tests (i.e., *Ceriodaphnia* bioassay tests) with more detailed analyses to determine whether the predicted instream biological impacts were actually occurring.

Text Table 1.	Frequency of positive invertebrate bioassay tests associated with sites at which no instream impact was observed.							
Location	Positive Number In-stream <i>Daphnia/Ceriodaphnia</i> of sites Non-impacted bioassay tests at %false examined sites non-impacted sites positives Reference							
North Carolina	43	12	3	25%	Eagleson et al., 1990			
Elkhorn Creek, KY	160	22	15	68%	Birge et al., 1989; Dickson et al., 1992			
Trinity River, TX	72	10	6	60%	Dickson et al., 1992			
CETTP (8 studies)	80	9	6	67%	Dickson et al., 1992			
Total =	355	53	30	57%				

In summary, given the demonstrated tendency for *Ceriodaphnia* tests to indicate toxicity in the absence of observable ecological effects in the field, the results of such bioassay toxicity tests should <u>not</u> be used as the only reliable evidence of instream biological impact. Bioassays were originally designed as "screening methods" to identify potentially toxic conditions, not as final quantitative indicators of ecological impacts. In addition, the available scientific data indicate that, contrary to the conclusions of EFED (pp 32-33), chlorpyrifos may play only a partial role in the bioassay mortality observed in estuaries around San Francisco, California.

E.2.1.3 Bioconcentration/Bioaccumulation of Chlorpyrifos (EFED p 33)

The EFED document notes (p 33) that fish residue data on chlorpyrifos have been collected in a nationwide monitoring study (U.S. EPA, 1992a). While the range of reported fish residues did vary widely from non-detectable or ND ($<0.05~\mu g/kg$) to 344 $\mu g/kg$, as stated in the EFED, it should be recorded the average chlorpyrifos concentrations for the different site categories (background, paper mills, refineries, industrial, and agricultural areas) were quite low, from ND (at Superfund sites and wastewater treatment plants) to 24 $\mu g/kg$ (agricultural sites). When examined as a cumulative frequency distribution on all 362 U.S. sites, the 90th and 75th percentile chlorpyrifos fish residue concentrations were approximately 11 and 0.8 $\mu g/kg$ (ppb), respectively, and \sim 75% of fish concentrations at all sites were below the analytical detection limit for chlorpyrifos (0.05 $\mu g/kg$). However, the EFED authors did not discuss the low magnitude and infrequent nature of the chlorpyrifos residues; it was merely noted that these data demonstrate "extensive off-field movement and exposure of chlorpyrifos to aquatic organisms."

It is disconcerting that EFED is willing to utilize field observations when adverse effects or field residues are observed, but fails to use the same information in refining their model predictions, i.e., the levels of chlorpyrifos residues in fish. The EFED authors were clearly aware of the nationwide fish monitoring study (U.S. EPA, 1992), but instead chose not to use this extensive database of fish residue values to refine their model predictions. On page 33 of the EFED document, the authors state that "chlorpyrifos residue levels in fish were estimated by multiplying the 21-day EEC from GENEEC model times the BCF values for whole fish (x2730) and viscera (x3900)." If we examine the GENEEC 21-day EEC values for a variety of agricultural sites and application rates (EFED p 26), the estimated pond water residues for chlorpyrifos range from 0.8 - 14.7 ppb. Using the resulting EFED model for chlorpyrifos residues in fish, these fish concentrations should vary from ~2 - 40 ppm in whole fish or from 3 - 57 ppm in viscera. A comparison of these residue estimates to the EPA-measured whole fish residues for chlorpyrifos at 362 U.S. sites (U.S. EPA, 1992) reveals the estimated fish residues exceeded the 90th percentile field concentration for chlorpyrifos (11 ppb) by 180 - 3600 times. Clearly, the use of the EFED model for chlorpyrifos residues in fish is inappropriate as it does not remotely

estimate the field concentrations of chlorpyrifos in fish tissue. Measured, probability-based residue values should be used in the EFED risk assessment calculations rather than grossly excessive estimated residues based on model-derived EEC values and a worst-case BCF value for chlorpyrifos.

The reasons for the EFED failure in vastly overestimating fish residues is clearly due to the elevated EEC values for chlorpyrifos, compared to field observations for aqueous residues. In addition, while the EFED document does note the rapid depuration of chlorpyrifos from fish tissue, the authors appear to misinterpret the implications of the extensive research on metabolism/elimination of chlorpyrifos in aquatic organisms. The available data indicate that the compound will quickly achieve steady-state residues in an exposed organism and residues will rapidly clear when the organism is placed in clean water; the measured fish first-order half-life for chlorpyrifos is 2 - 3 days (Murphy and Lutenske, 1986). However, the EFED authors did not mention the findings of Murphy and Lutenske (1986), who established that ~25% metabolism of the ¹⁴C-labeled chlorpyrifos (28-day water exposure) occurred in the rainbow trout, with TCP and two other polar metabolites as the principal degradates. In an experiment dealing with waterborne exposure of chlorpyrifos (uncited by EFED), Barron et al. (1993) studied the pharmacokinetics of uptake and metabolism in the channel catfish. Chlorpyrifos was primarily eliminated from the catfish by biotransformation, with TCP constituting the major metabolite in the blood (~40% of total residues), and the glucuronide conjugate of TCP was the major metabolite in urine (60-90%) and bile (90%). In both this work and an earlier study on the dietary exposure of chlorpyrifos in catfish (uncited by EFED - Barron et al., 1991), the authors found the metabolism of chlorpyrifos in catfish to be similar to that measured in other species of fish and mammals. Barron et al. (1991) reported "Extensive metabolism resulted in a low potential for chlorpyrifos to accumulate in catfish from dietary exposure."

Similar findings were noted by Woodburn et al. (1995) following dietary exposure of chlorpyrifos to catfish (uncited in EFED); the chlorpyrifos fish residues accumulated via the food chain were 20% or less of the concentration of the compound in foodstuffs, i.e., bioaccumulation was not

occurring via the food chain. Cumulatively, these data contradict the EFED assumption (p 33) that chlorpyrifos may bioaccumulate into fish, mammals, and birds feeding on aquatic organisms in chlorpyrifos-contaminated habitats: "Fish and other aquatic organisms may bioaccumulate chlorpyrifos residues from the water, sediments, and/or their food. Chlorpyrifos residues in aquatic organisms are a route of exposure for birds and mammals, which feed on these aquatic organisms." Indeed, the data clearly show that chlorpyrifos possesses a sufficiently high metabolism/elimination rate in aquatic organisms that bioaccumulation into higher trophic levels should not be an issue of concern (Thomann, 1989; Thomann et al., 1992).

E.3 Aquatic Incident Reports

p 27. "Dramatic declines in amphibian populations have been reported nationwide. There is no direct evidence to show that chlorpyrifos is responsible for the decline in amphibian populations. However, in the case of chlorpyrifos, the tadpole state of some toads is as sensitive as bluegills and the field studies reported chlorpyrifos-related deaths of an adult frog and toad."

First, there is no evidence, scientific or otherwise, that the use of chlorpyrifos is responsible for the global decline in amphibian populations. This trend is observed even in areas where chlorpyrifos usage is minimal or non-existent. Johnson and Prine (1976) have examined the effects of an exposure of chlorpyrifos on hydrated and dehydrated juvenile western toads (*Bufo boreas*). This work indicates that aquatic doses of 30 and 60 ppb are not toxic ("sublethal concentrations") to either hydrated or dehydrated juvenile western toads. These western toads were juvenile in growth stage (approx. 2 cm long) and the data indicate this species of toad is not highly sensitive to aquatic dose concentrations in the low ppb range. Thus, to make such a broad statement on global decline in amphibian populations resulting from chlorpyrifos exposure based on a single study that found one dead frog/toad is only conjecture, is not sound science, and would certainly not stand-up to a credible peer review. Statements such as these from a scientific chapter should be avoided unless there is data which can substantiate the claim.

Dow AgroSciences has analyzed all known surface water contamination incidents involving fish kills that resulted from legal use of products containing chlorpyrifos. Because there are no references for any of the freshwater incident reports summarized by EFED, it is difficult for Dow AgroSciences to determine whether the database reviewed by EPA duplicates our information.

As EFED recognizes in the draft science chapter, most of these relatively few incidents are related to termiticide applications. The draft EFED science chapter made references to reported detection of chlorpyrifos in surface water following a termiticide application. These references failed to recognize surface water detection of chlorpyrifos has previously been identified by the EPA OPP as an industry issue related to the use of all products as liquid, soil-applied termiticides. This recognition led to the issuance of PR Notice 96-7 (EPA 730-N-96-006 – dated October 1, 1996) which required all manufacturers of liquid termiticides to adopt common label use directions which would reduce even further the low probability of water contamination regardless of the termiticide used.

In the paragraph starting on the bottom of page 92 and ending on the top of page 93 discussing estuaries, it is unfortunate that EFED emphasizes hazard and not risk. This paragraph clearly states that although "chlorpyrifos contamination exists in estuarine areas" and "chlorpyrifos was rated as one of the most hazardous pesticides in NOAA inventory using the hazard rating system," "chlorpyrifos was responsible for only a few fish kills." Therefore, while chlorpyrifos is detectable in some estuarine ecosystems, the concentrations are apparently not high enough to cause widespread or repeated incidents of mortality.

The definition of an insecticide is a chemical that kills insects. Dow AgroSciences is not familiar with any insecticide that does not adversely affect any non-target organisms. Chlorpyrifos is highly toxic to many aquatic organisms. Therefore, it is not surprising that there are some reports of aquatic incidents. It should be noted, however, that after more than three decades of chlorpyrifos use and numerous applications, relatively few aquatic incidents have occurred. In a

weight-of-the-evidence, risk/benefit analysis, chlorpyrifos clearly does not cause the widespread and repeated mortality predicted by the EFED screening level assessments.

E.4 Aquatic Effects in Terrestrial Field Studies

p 57, 1st paragraph: "It was reported that, 'Dead fish were found in ponds adjacent to citrus groves on several occasions during the field portion of the study. The dead fish were collected and shipped to the Sponsor. Additional samples and information collected in association with the dead fish (i.e., water and sediment samples, water temperature and dissolved oxygen) were also forwarded to the Sponsor. Since the objectives of the study did not address aquatic organisms, the fish and other aquatic vertebrates found during the study are not reported in this report. The responsibility for reporting the dead fish and other aquatic vertebrates found during this study was left with the Sponsor.' Information on chemical analyses of fish and other aquatic vertebrate, sediment, and water samples have not been received from the Sponsor for review."

This statement is incorrect. A 6(a)(2) report was submitted to OPP on 15 July 1992. A summary follows: Fish were found dead in two ponds following airblast application of Lorsban 4E insecticide. Both ponds were slightly elevated above the orange grove. Surrounding the ponds were eucalyptus and a single row of citrus trees. While the Lorsban 4E label has the following precautionary notice "This pesticide is toxic to birds and wildlife, and extremely toxic to fish and aquatic organisms. Do not apply directly to water. Drift and runoff from treated areas may be hazardous to aquatic organisms in adjacent aquatic sites.", the single row of citrus trees were sprayed and direct application was observed into the ponds. Subsequent analysis of the water, sediments, and fish samples confirmed the presence of chlorpyrifos. It should be noted that this orange grove, except for the single row of citrus trees around the ponds, had been treated approximately one month earlier with Lorsban 4E at a rate of 7 pt/A in a spray volume of approximately 140 gal/A without any incident. This fact, in conjunction with evaluation of the events resulting in this incident, indicates that the pond contamination and resultant aquatic wildlife mortality was a consequence of direct application into the ponds and not runoff or leaching through soil.

p 60, 1st paragraph: "'On several occasions fish were found dead in water hazards during the study, some of which were found in the study area and some which were found outside of the study area on test golf courses. The Sponsor was notified of the occurrence and provided with water, sediment and fish samples. Any fish collected were shipped to the Sponsor for evaluation

along with fourteen water samples and twelve sediment samples collected from water hazards where fish were found. Since the study deals with terrestrial hazard and was not structured to evaluate aquatic hazard, the responsibility for reporting these occurrences was left with the Sponsor and are not discussed in this reported.' Information on chemical analyses of the samples of fish, sediments, and water have not been received by EFED for review."

This information is misleading. While it cannot be proven that chlorpyrifos did not contribute to the deaths of the fish in the turf study, the following factors suggest that this is highly unlikely:

- (1) A total of 192 water samples (96 from both liquid and granular treatment replicates) were collected from water hazards in the golf courses. On liquid treatment replicates, no chlorpyrifos residues were detected in any of the samples. On granular treatment replicates, residue values from all but two samples (1.7 ppb on site G5 and 2.5 ppb on site G8) were less than the LOQ and only occurred immediately following the second application (see Table 15 of the turf study).
- (2) Acephate, another organophosphorus insecticide, as well as a variety of other pesticides (see Appendix III of the turf study) were used intermittently with chlorpyrifos.
- (3) There was an unusual amount of inclement weather on the golf courses during this study (presumably as a result of Hurricane Andrew) that may have caused or contributed to the incidental fish kills.

Appendix F: Terrestrial Effects Profile

F.1 Terrestrial Laboratory Studies

Information concerning terrestrial effects is provided throughout EFED's science chapter. This appendix provides the comments of Dow AgroSciences on terrestrial effects. Specifically, we provide a discussion of errors, omission of studies and other relevant information, as well as provide comments on interpretation of the data.

F.1.1 Errors

- 1. In the table on page 19 the correct spelling for the scientific name for the rock dove is *Columba*, not *Columbia*.
- 2. On pages 19 and 20 EFED presents a table to illustrate the number of chlorpyrifos granules/LD₅₀. Inexplicably, EFED selected toxicity values for technical chlorpyrifos rather than use values for the formulated granules. EFED acknowledges (p 41) that "...granular chlorpyrifos products...are less toxic (i.e., less hazardous) than technical grade chlorpyrifos." Dow AgroSciences therefore suggests that the table on page 19 represent toxicity to granules based on empirical data rather than the incorrect assumption by EFED that the toxicity of technical chlorpyrifos is representative of granular product.. Thus the table on page 19 should be revised based on the available data (see p 45 of the EFED document and Appendix F of this response). For species that do not have toxicity data for the granular formulations, we chose EFED's approach of selecting the most sensitive value on an mg a.i./kg body weight basis as representative of the toxicity of untested species. These data illustrate the low risk of granular chlorpyrifos, thus explaining the lack of avian and mammalian incidents specific for granular formulations. The revised table is presented below.

Granular Risks to Wildlife Expressed as Number of Granules per LD_{50} . Toxicity to untested birds assumed to be equivalent to the most sensitive species tested, the rock dove; while mammals are assumed to be as sensitive as female rats. Species tested with granular formulations are in bold. (Lorsban 15G average weight is $0.064 \, \text{mg/granule}$ and contains $0.0096 \, \text{mg}$ a.i.chlorpyrifos per granule)

formulations are in bold. (Lorsban 15G average weight is 0.064 mg/granule and contains 0.0096 mg a.i.chlorpyrifos per granule)								
Species	LD ₅₀ (mg a.i./kg body wt.)	Body Weight (kg)	mg/LD ₅₀	Granules/LD ₅₀				
House Sparrow Passer domesticus (MRID 44057101)	111	0.025	2.77	289				
Rock Dove ^A Columba livia (MRID 00045891)	54	0.350	18.9	1,969				
Ringe Turtledove ^A Streptopelia risoria Hill & Camardese, 1984	157	0.150	23.5	2,448				
Bobwhite Quail Colinus virginianus Hill & Camardese, 1984, Cited by Smith, 1987 MRID41043901)	108	0.178	19.2	2000				
Rat (Female) Rattus norvegicus (MRID 44248604)	193	0.124	23.9	2,490				
Rat (Male) Rattus norvegicus (MRID 44248604)	337	0.170	57.3	5969				
Common Grackle Quiscalus quiscula	54	0.114	6.2	645				
Red-winged Blackbird Agelaius phoeniceus	54	0.0526	2.8	292				
Mammal (15 g body wt.)	193*	0.015	2.9	302				
Japanese Quail Coturnix japonica	54	0.178	9.6	1000				
Mammal (35 g body wt.)	193	0.035	6.8	716				
Starling Sturnus vulgaris	54	0.0823	4.4	458				
Ring-necked Pheasant Phasianus colchicus	54	1.135	61.2	6,375				
Rat Rattus norvegicus	193	0.200	48.2	5,021				
Mallard Duck Anas platyrhynchos	54	1.082	58.4	6,083				
Mammal (1000 g body wt.)	193	1.000	193	20,104				

^aThis study was included as an example of granular toxicity recognizing that the number of birds used during the test (5 for the rock dove and 8 for the ringed turtledove) was too few to meet guideline requirements. However, they contribute to the "weight of the science" on the toxicity of granular chlorpyrifos to birds.

3. The draft science chapter states on page 20:

"But for species as sensitive as the house sparrow, consumption of relatively few granules may be needed to produce lethal effects (i.e., only 29 granules are needed to exceed its LD_{50} value)."

The acute toxicity of the granular formulation of chlorpyrifos, Lorsban 15G granular insecticide, to the house sparrow was experimentally determined and reported by Gallagher et al., 1996, MRID 44057101. The LD₅₀ obtained corresponds to ca. 289 granules, a factor 10 more granules than the 29 predicted based upon the experiments with technical chlorpyrifos reported in Schafer and Brunton, 1979, MRID 40378401.

4. The draft science chapter states on page 20:

"For example, if a 70 to 80-gram bird consumed eight earthworms with an average of 6 to 10 granules attached to or inside each earthworm, the exposure would be equivalent to the house sparrow LD_{50} value."

This statement is incorrect. Based on scientifically sound empirical data on the toxicity of Lorsban 15G insecticide to the house sparrows (289 granules), it would require over 800 granules to achieve an LD₅₀ for a similarly sensitive 75-g bird. However, EFED's statement is speculation. No data are presented, and Dow AgroSciences is unaware of any data, to support the contention that granules sticking to soft-bodied invertebrates are consumed by animals incidental to the consumption of the invertebrates.

5. On page 41 the EFED states that

"The risk assessment endpoint for avian reproduction is a NOEC of 25 ppm based on the mallard duck study showing 84 percent reduction in the number of eggs and 89 percent reduction in the number of young."

Dow AgroSciences believes that this statement would be more correct if the statement were revised to: The risk assessment endpoint for avian reproduction is a NOEC of 25 ppm based one of three mallard reproduction studies in which the LOEC of 125 ppm was maternally

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toxic, which led to an 84% reduction in the number of eggs and an 89% reduction in the number of young.

6. On page 44 EFED states

"Second, all passerine species tested are included in this grouping (i.e., grackle, sparrow,

This statement is in error. The starling is also a passerine and it is not included in the group of more sensitive birds. The obvious typo, blackwing blackbird, should be corrected to redwinged blackbird.

7. There is an error in the table on page 51 presenting the Mammalian Acute Oral Toxicity Findings. In reporting the toxicity of Dursban* 2E specialty insecticide to the rat (MRID 00000186) the percent a..i. and the calculated LD₅₀ values are incorrect. These data are from Carreon et al., 1982 (MRID 00120262). The test material was 25.6% active, not 22.4 % as stated in the table. As such, the correct LD₅₀ values should be 300 mg a.i./kg for males and 196 mg a.i./kg for the females.

8. In discussing earthworm toxicity (pp 53-54), the EFED stated

"Two supplemental published articles reported effects on earthworms in chlorpyrifos-treated trefoil pastures. Thompson (1972) reported no significant effects on earthworms in trefoil pastures after applying Dursban 2 EC at 2.0 lbs/A. Three weeks after treatment earthworms averaged 14.1 worms per quadrant and 343.5 grams fresh weight per quadrant compared to control averages of 17.9 worms and 404.6 grams, respectively. (MRID 00078524). Thompson and Sans (1974) reported results on earthworms in a southwestern Ontario trefoil pasture after a spray treatment with a chlorpyrifos EC at 2 lbs ai/A. At 3 and 52 weeks post treatment, the mean number of earthworms and mean biomass per quadrant were 2.56 (± 3.65) worms and 2.73 (+ 3.54) grams, respectively (controls were 2.85 (+ 3.58) worms and

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^{*} Trademark of Dow AgroSciences LLC

2.94 (\pm 3.29) grams, respectively). Chlorpyrifos residue levels in earthworms 3 and 52 weeks post-treatment were 9.66 ppm and 0.0 ppm, respectively. (MRID 00095371). While the results from these two studies were not dramatic enough to be statistically significant (p = 0.05), the results in **both** studies indicate consistent reductions in the numbers of worms and reductions in fresh weight measurements compared to controls.

The above statement is a misrepresentation of the author(s) conclusions and the data. Thompson (1972) commented that "Dursban...had no effects on numbers or biomass that could be assessed in this experiment." It should be noted that, of the nine compounds tested, six had a 55% or greater reduction in worm numbers and a 40% or greater reduction in biomass, much greater than chlorpyrifos. The EFED also failed to report Thompson and Sans (1974) found that after one year, both mean number of worms per quadrant and mean biomass per quadrant increased in the chlorpyrifos treated plots when compared to the controls. Thompson (1972) pointed out that "Numbers alone do not present a true record of the effects of pesticides. The biomass is more important...." A more in-depth analysis of Thompson and Sans (1974) data shows that the difference between the chlorpyrifos and the controls in terms of biomass was a 0.21 g reduction at three weeks and a 0.3 g increase at 52 weeks. Perhaps the "consistent reduction" claimed by the EFED actually represents inherent variability in sampling, accounting for the lack of statistical significance in both studies.

9. On page 73 in the table concerning amphibian toxicity findings, the EFED states in the toxicity category that for three of the values, chlorpyrifos is *at least moderately toxic*.

Dow AgroSciences is not aware of this classification in any official EPA communications. What was the basis for this statement?

F.1.2 Omissions

There are several studies that have not been cited by EFED. These data are provided below. Dow AgroSciences considers these data relevant to the discussion of the hazard of chlorpyrifos to birds, but does not endorse these studies from a data quality perspective.

F.1.2.1 Acute Oral Avian

Acute Oral Toxicity of Chlorpyrifos to Avian Species

Common Name	Age	Purity %	LD50 (mg a.i./kg)	95% C. I.	Slope	Author
American crow	N. R.	Technical	>32	N. R.	N. R.	Schafer, 1972
Beltsville small white turkey	6-7 weeks	Technical	32-63	N. R.	N. R.	Stevenson, 1967a MRID 0095285
Broad-breasted white turkey	4 weeks	25.0	20-40	N. R.	N. R.	Schlinke et al., 1969
Common grackle	N. R.	94.5	13.0	N. R.	N. R.	Schafer and Brunton, 1971
Leghorn cockerel	6 weeks	Technical	50-63	N. R.	N. R.	Stevenson, 1967b MRID00095120
Leghorn cockerel	10-12 days	98+	25.4	20.8-30.9	N. R.	Sherman et al., 1967
Leghorn cockerel	N. R.	Technical	31.6	N. R.	N. R.	Stevenson, 1963 MRID00095286
Mallard	36 hr	94.5	145.0	55.8-377	N. R.	Hudson, R. H. et al., 1972 MRID 00102038
Mallard	7-8 days	94.5	29.4	18.6-46.7	N. R.	Hudson, R. H. et al., 1972 MRID 00102038
Mallard	30-33 days	94.5	50.4	32.5-78.1	N. R.	Hudson, R. H. et al., 1972 MRID 00102038
Mallard	6 months	94.5	83.3	44.0-158	N. R.	Hudson, R. H. et al., 1972 MRID 00102038
Northern bobwhite	19 weeks	75.5	53.0	40-76	N. R.	Pederson, 1996b
Red-winged blackbird	N. R.	94.5	13.3	N. R.	N. R.	Schafer and Cunningham, 1972
Ringed turtledove	N. R.	15 Granular	157.0	123-200	4.40	Hill and Camardese, 1984
Rock dove	N. R.	5 Granular	54.0	498-2398	N. R.	Ross et al., 1976 MRID 00045891

N.R. = Not Recorded

F.1.2.2 Acute Dietary LC₅₀

The following table provides additional acute dietary toxicity data. Dow AgroSciences considers these data relevant to the discussion of the hazard of chlorpyrifos to birds, but does not endorse these studies from a data quality perspective.

Acute Dietary Toxicity of Chlorpyrifos to Avian Species

Common Name	Age	Duration	Purity (%)	LC50	95% C. I.	Slope	Author
Mallard	14 days	8 D	Technical	1080	707-2503	0.954	Gile et al., 1983
Mallard	14 days	8 D	Technical	900	746-1255	1.796	Gile et al., 1983
Mallard	14 days	8 D	Technical	757	478-1443	0.892	Gile et al., 1983
Mallard	14 days	8 D	Technical	671	322-2170	0.615	Gile et al., 1983
Mallard	5-7 days	8 D	Technical	180	150-220	N. R.	Shellenberger, 1970
Northern bobwhite	14 days	5 D	94	647	564-737	8.1	Bennett, 1989a
Northern bobwhite	14 days	8 D	Technical	392	293-522	1.937	Gile et al., 1983
Northern bobwhite	14 days	8 D	Technical	421	332-535	3.142	Gile et al., 1983
Northern bobwhite	14 days	8 D	Technical	353	294-429	N. R.	Gile et al., 1983
Northern bobwhite	14 days	8 D	Technical	397	318-498	3.753	Gile et al., 1983
Northern bobwhite	14 days	8D	94	851	N. R.	N. R.	Shirazi et al., 1994
Northern bobwhite	14 days	28D	94	478	N. R.	N. R.	Shirazi et al., 1994
Northern bobwhite	16 weeks	28D	94	1100	N. R.	N. R.	Shirazi et al., 1994

N. R. = Not Recorded

F.1.2.3 Toxicity of Formulations

- 1. The toxicity of Lorsban 15G granular insecticide to the Ringed Turtledove (*Streptopelia risoria*) was evaluated by (Hill and Camardese, 1984). Groups of eight birds were dosed with one of five test concentrations. The LD₅₀ was determined to be 157 mg a.i./kg, with 96% confidence interval of 123 200 mg a.i./kg.
- 2. Ross, et al (1976) (MRID 00045891), exposed the common pigeon to Dursban 5% granules. There were five birds per dose level. The LD₅₀ was determined to be 1083 mg/kg expressed as the granular formulation ,or 54 mg a.i./kg. Comparative data on the toxicity of the technical material to the pigeon has been reported to be from 10 (MRID40378401) to 26 mg/kg (MRID 00160000), indicating that the granular formulation is less toxic on an mg a.i. basis than the technical material.

The granular studies cited above were included as examples of granular toxicity, recognizing that the number of birds used during the tests was too few to meet guideline requirements. However, they contribute to the "weight of the science" on the toxicity of granular chlorpyrifos to birds.

F.1.2.4 Avoidance and Behavior

The EFED reviewed several papers dealing with special tests. Dow AgroSciences wishes to provide additional data related to avoidance of chlorpyrifos which demonstrates many species of birds avoid chlorpyrifos-contaminated feed that may lead to a reduction of exposure in field applications.

1. The hypothesis that pheasants can detect chlorpyrifos-treated food and that they will reduce food consumption unless an untreated choice is available was tested by Bennett and Prince (1981). Prior to testing, food consumption was recorded for year-old pheasants provided 150 g of an equal mixture of corn and commercial diet. Following this acclimation period, birds were provided with 150 g of a mixture of commercial diet and corn either treated with

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2,200 mg/kg a.i. chlorpyrifos or a choice of untreated food and treated food. Birds provided with chlorpyrifos-treated food only reduced food consumption to 10% of that during the pretreatment period. Birds given a choice between treated and untreated food did not show a difference in food consumption when compared to the pre-treatment period. Consumption of the chlorpyrifos-treated food ceased after one or two days. Other experiments determined the preferred food (commercial feed, whole corn, wheat or oats) of the pheasant and the food selection when the preferred food was treated with chlorpyrifos. The results indicate that pheasants will detect and avoid preferred food treated with chlorpyrifos if suitable but less preferable alternatives exist. Therefore, if not all food items are contaminated, pheasants and presumably other birds will avoid contaminated food and seek out alternative food sources.

2. In five-day dietary tests in which there was a choice of chlorpyrifos treated and untreated diet, the discrimination threshold (DT), defined as the dietary concentration above which the birds discriminated between treated and untreated food by consuming a greater proportion of untreated food, was determined (Bennett and Schafer, 1988; Bennett, 1989a,b). Fourteen-day-old northern bobwhite were tested in each of the following designs: a) one feeder per cage with treated food; b) two feeders per cage - one with treated food and one with untreated food; c) 10 feeders per cage - five treated and five untreated; and, d) 10 feeders per cage - nine treated and one untreated. Food consumption, signs of toxicity and mortality were monitored. The LC₅₀ in the treated food only test was 647 mg/kg. The DT occurred at sublethal dietary concentrations in all chlorpyrifos tests (DT = 45 mg/kg in the 1:1 test; 24 mg/kg in the 5:5 test; and, 69 mg/kg in the 9:1 test. If one calculates a ratio of the LC₅₀/DT for chlorpyrifos (e.g., 647/69), a margin of safety of 9.4 is obtained. These data demonstrate that birds will likely avoid chlorpyrifos contaminated food items at concentrations well below LC₅₀ concentrations.

These data indicate that chlorpyrifos has intrinsic repellent properties or results in conditioned aversion. The mitigation of exposure as a consequence of these properties is an important principle to consider when evaluating the risk of chlorpyrifos to birds. In fact, this may be a

factor in the lack of widespread accounts of avian mortality in contrast to the high level of risk assumed in EFED's Tier I risk assessment.

F.1.3 Data Quality and Interpretation

F.1.3.1 Acute LC₅₀ Values

On page 41 EFED states "Numerous subacute dietary LC_{50} values are available, but the data are limited to dietary toxicity data for only four avian species. The lowest avian subacute LC_{50} value used for assessing dietary risks is 136 ppm for mallard ducklings (moderately toxic).

There are three acute LC_{50} values provided for the mallard. Ideally, if there is more than one toxicity value for a given species and there is reasonable assurance of data quality for each value, the geometric mean of these values represents a conservative estimate of the "true" sensitivity of the species and should be used when conducting risk assessments (U.S. EPA, 1995c).

F.1.3.2 Acute Oral Toxicity

On pages 41-47, EFED provides a summary of acute oral and acute dietary toxicity data on different species of birds. In many cases the data are cited from secondary and tertiary sources. Use of such data raises a high level of concern within Dow AgroSciences as to the appropriateness of the data for use in a risk assessment of this magnitude. For these studies EFED did not have the original data for statistical analysis to "validate the conclusions" nor assess the experimental design. This oversight by EFED is repeated throughout this section and is exemplified by the citations of Smith, 1987; Hudson et al., 1984; and, Schafer and Brunton, 1979. Below are some of the more egregious examples.

1. The acute LD₅₀ value for the ring-necked pheasant is cited from Hudson et al. (1984) (MRID 00160000). Hudson et al., 1984 is a compilation of data generated "over a number of years" at the Denver Wildlife Research Center. Much of the information in this document had been published earlier by a number of authors. The data for the pheasant was first published by Tucker and Haegele (1971). These studies were conducted with three to seven birds at each

dose group. It is unclear how many pheasants were tested with chlorpyrifos or the nature of the dose response. Despite these failings this study was judged "core" by EFED! Clearly, a study submitted by a registrant with this lack of specificity and adherence to approved protocols would be unacceptable (EPA, 1982). Note that on page 49 EFED pointed out for two studies submitted by Dow AgroSciences that the raw data were "unavailable for complete evaluation" of the studies. This caveat should be provided for all of the studies cited from secondary sources.

2. A clear example of EFED's disregard for data quality analysis and its selective use of data deals with the acute oral toxicity data for the house sparrow. On page 43 EFED cites three studies on the toxicity of chlorpyrifos to house sparrows: Schafer and Brunton (1979, MRID 4037840); Hudson et al. (1984, MRID 00160000); and, Gallagher et al. (1996, MRID 44057102). EFED elected to use the data of Schafer and Brunton (1979, MRID 40378401), an LD₅₀ of 10 mg/kg, as the value to be used in the risk assessment. The methods followed during the conduct of this study included the ASTM Recommended Practice for Determining Acute Oral LD₅₀ for Testing Vertebrate Control Agents (E555-75) and methods described by Schafer et al. (1973). The ASTM methodology is quite brief and provides no guidance on the appropriate number of test animals; however, Schafer et al. (1973) methodology indicates that two birds were used at each test level, which is far fewer subjects than required by EPA guidelines or for acceptable statistical analysis. The source of the sparrow data in Hudson et al. (1984) is Tucker and Haegele (1971). These authors indicated that for the chemicals tested, three to seven birds were used at each treatment level; it is unclear how many birds were used at each dose level in their test with Dursban. This uncertainty raises serious doubt as to the applicability of the data. Based on the citation (a secondary source), it is clear the raw data were not reviewed by EFED to validate the results. The study by Gallagher et al. (1996) was conducted under GLP and followed stringent EPA guidelines. The validity of this study has been verified by EFED. Surprisingly, EFED chose the data from Schafer and Brunton (1979) in the evaluation of the risk of chlorpyrifos to birds. Dow AgroSciences considers the use of Schafer and Brunton's (1979) data and the exclusion of recent

scientifically sound data (Gallagher et al., 1996) in its risk assessment to lack scientific or regulatory justification. Simply to use the lowest LD₅₀ value for a species, without considering its scientific merit, is scientifically unsound. Ideally, all of the data should be considered. Unfortunately, the Tier I assessment (the use of the simple quotient method) may preclude this option. As such, the only scientifically sound option is to use the only scientifically validated study in the risk assessment; that is, the study of Gallagher et al. (1996).

- 3. Dow AgroSciences also notes the data for the common grackle is from Schafer and Brunton (1979) and suffers from the same deficiencies as their sparrow data.
- 4. The draft science chapter states on page 44:

"Two factors are common to this grouping. First, in general, these birds are are (sic) smaller body weights than the other avian species, which agrees with the scaling factors proposed by Mineau et al. (1996)."

Given that large and small birds are represented in both the sensitive and insensitive classes, and that the absolute toxicity values are imperfectly known, an unbiased observer would see no convincing relationship between body weight and toxicity. To claim that the table, as presented on page 44, supports the scaling factors presented in Mineau is unfounded. No body weights are given and no direct calculation and subsequent verification of toxicity values obtained using Mineau's suggested scaling is attempted. Without further discussion of how such a scale factor would affect the interpretation of the chlorpyrifos toxicity data, the question of the validity of the scale factor is moot.

F.1.3.3 Toxicity of Formulations

On pages 44-45, EFED provides data on the acute oral toxicity of formulations to the bobwhite and house sparrow. The source of the bobwhite data is give as Smith (1987, MRID 41043901). These data are from Hill and Camardese (1984). These authors determined the LD₅₀ for Lorsban 15G granular insecticide to be 108 mg/kg. The pesticide was administered as percent a.i. based

on an average granule weight of 0.064 mg with 15 % chlorpyrifos/ granule. These data indicate that for the bobwhite to achieve an LD_{50} it would have to ingest ~2,000 granules! These authors also tested the ringed turtledove and reported that the LD_{50} of Lorsban 15G granular insecticide was 157 mg/kg. This is equivalent to ingesting over 2,000 granules. The authors concluded that for these species the granular formulation of chlorpyrifos was significantly less toxic than technical chlorpyrifos.

The study by Gallagher, et. al (1996, MRID 44057101) also provides the toxicity of Lorsban 15G granular insecticide as percent a.i. as well as in the number of granules administered. The LD_{50} of approximately 111 mg a.i./kg is equivalent to 289 granules. There was 10% mortality at 100 granules per bird and no mortality at 50 or 25 granules per bird.

EFED based its risk assessment of granular formulations on the ingestion of granules by birds and mammals. Dow AgroSciences believes the above data are critical to the evaluation of granule toxicity to birds and the use of toxicity data on the technical material is not relevant in the assessment of granular risk.

<u>F.1.3.4</u> Mammals, Acute and Subacute Toxicity (pp 50-52)

Some of the same problems that were apparent with the avian toxicity data also occur within this section.

For example, under Mammalian Acute Oral Toxicity Findings, the rat toxicity data, LD₅₀ 97-276, cited from Smith, 1987 (MRID 41043901) is actually a tertiary source for this information. Smith (1987) cites the 1982 version of the "Farm Chemicals Handbook" (Berg, 1982), which is, at best, a secondary source of information itself, as the source of these data. Clearly, these data could not possibly have undergone a quality check to validate the findings. EFED uses the LD₅₀ value of 97 mg/kg in its assessment of risk simply because it was lowest reported value. There is no credible regulatory or scientific justification for EFED to use unverifiable data from a tertiary source in its risk assessment while ignoring studies that have undergone regulatory review. Dow AgroSciences strongly objects to EFED's subjective use of such data.

F.1.3.5 Select Toxicity Values for Risk Assessment (p 103)

F.1.3.5.1 Mammalian Toxicity Values and Conversions

EFED chose to use the LD₅₀ of 97 mg/kg because it was the "lowest mammalian acute LD₅₀ value." As mentioned above, this value is from a tertiary source and has no documentation on methodology or dose response data to verify the findings. Dow AgroSciences strongly objects to EFED's use of a single, quality insensitive, criterion such as "lowest mammalian acute LD₅₀ value" without due regard to the integrity of the data. This subjective approach is inconsistent with the Agency's stated position that each report "should include all information necessary to provide a complete and accurate description of test procedures and evaluation of the test results" (U.S. EPA, 1982). Furthermore, Standard Evaluation Procedures (SEP) have been developed by the EPA to ensure "...comprehensive and consistent treatment of the science in reviews..." of data used in risk assessments (Urban and Cook, 1986).

EFED used lowest mammalian acute oral LD_{50} value to calculate estimated 1-day LC_{50} values. This procedure should only be used when no LC_{50} values are available and then with "reservation and restrictions" (Urban and Cook, 1986). Dow AgroSciences provides a more scientifically sound approach, based on the recommendations of the EPA (Urban and Cook, 1986), to calculate 1-day LC_{50} values.

Therefore, Dow AgroSciences proposes the narrative and table on page 104 be amended as follows:

Assessment of risks to small mammals potentially exposed to residues on food items requires that the acute dietary LC_{50} value be converted to mg/kg/day to estimate daily exposure. The geometric mean of the five valid rodent LC_{50} value 2027 ppm (pp 51-52) was used as the reference LC_{50} value. To estimate daily LC_{50} concentrations for a variety of small to medium-sized mammals having different dietary needs, it is assumed that each species has the same sensitivity as the laboratory rat (e.g., LC50 = 2027 ppm). The laboratory rat was assumed to weigh 150 g and consume 10% of its body wt day⁻¹. The following formula was used to calculate the unknown LC_{50} values in mg/kg/day (Urban and Cook, 1986)

 $LC_{50}(mg/kg/day)_{untested\ species} = \underline{LC_{50}\ (mg/kg)\ tested\ species}\ x\ food\ consumed\ as\ \%\ body\ wt\ day^{-1}\ tested\ species}$ food consumed as % body weight day $\frac{1}{2}$ untested species

The following table provides mammalian LC_{50} values to be used in subsequent risk assessments.

Estimated LC_{50} values based on a reference rodent LC_{50} of 2027 ppm. Assuming untested species have the same sensitivity as the laboratory rodent and that the laboratory rodent weighs 0.150 kg and consumes 10% of its body weight day⁻¹

Mammalian Species	Body Weight (g)	% Body Wt Consumed per day	Est. 1-day LC50 ppm
Herbivores/Insectivores	15	95	213
	35	66	307
	1000	15	1,351
Granivores	15	21	965
	35	15	1,351
	1000	3	6,757

F.1.3.6 Avian Toxicity Values

In the selection of the avian acute LD₅₀ value for the sparrow of 10 mg/kg, EFED violated clear EPA policy of using scientifically validated data. It is obvious that EFED's policy was to create the most conservative risk assessment regardless of the scientific merits of the decision. Dow AgroSciences strongly objects to EFED's use of a single, quality insensitive, subjective criterion to choose data for a risk assessment. This subjective approach is inconsistent with stated Agency position that each report "should include all information necessary to provide a complete and accurate description of test procedures and evaluation of the test results" (U.S. EPA, 1982). Furthermore, SEP have been developed by the EPA to ensure "...comprehensive and consistent treatment of the science (emphasis added) in reviews..." of data used in risk assessments (Urban and Cook, 1986). The reports for the house sparrow and for the common grackle do not approach meeting these standards and should not be used in a Tier I risk assessment.

F.2 Terrestrial Field Studies

F.2.1 Correction of Errors

F.2.1.1 Large Pen, Simulated Field Study

p 54, 2nd paragraph under Terrestrial Field Studies: "Results indicated that a rash of control mortality occurred at the end of the study. Of the 6.2 % control deaths, 67% occurred during the last five days. In the low treatment, 82% of the 7.6 % deaths occurred during the same period. In contrast only 29% of the 10 % mortality in the 6-lbs ai/A occurred during that same period. The degree of mortality attributable to chlorpyrifos in the treatments is uncertain. If mortality occurring during the last five days of the study were omitted, mortality in the high treatment might be statistically significant. The NOEL and LOEL for this turf study are 3 and 6 lbs ai/A, respectively, based on abnormal behavior and mortality."

The NOEL and LOEL are based only on abnormal behavior and the rationale presented by EFED is scientifically unsound. The implication that something other than chlorpyrifos was responsible for the deaths of the birds in the control and 3 + 3 lb a.i./A treatment groups, whereas the mortality resulting in the 6 lb a.i./A treatment group was due to the treatment, is unfounded. Since the birds from each of the groups came from the same game farm, were given the same type of feed and water, were exposed to the same types of conditions, and due to the large number of birds and replicates per treatment (16 birds x 9 replicates = 144 birds per treatment), the birds in the 6 lb a.i./A treatment should have also experienced a "rash of mortality at the end of the study" which may have caused the 6 lb a.i./A treatment to be statistically different from the control and 3 + 3 lb a.i./A treatment groups. However, this was not the case. A similar study using 8 - 18 week old turkeys held in pens for four weeks with soils treated with 0, 4, 8, 16, and 32 lb a.i./A found no toxicological hazard at any application rate (Kunz and Radeleff, 1972). Also, up to 10% mortality is generally acceptable in control groups conducted under EPA guidelines (U.S. EPA, 1996a, b). In this study, neither the control nor the treatment groups exceeded 10% mortality. Therefore, it is not surprising that mortality was not statistically different when the control and treatment groups were compared.

F.2.1.2 Iowa Corn Study

The draft science chapter states on page 20

"Chlorpyrifos-related mortality of both birds and small mammals in field studies were reported for granular applications on corn and golf courses."

No birds found dead contained a detectable chlorpyrifos residue following granular applications on corn or golf courses. There were no mammalian casualties found following the granular treatments in the Florida golf course study. There was one mammal found dead with a chlorpyrifos residue following the nine applications of granular chlorpyrifos to Iowa corn fields.

The draft science chapter states on pages 54-55

"Field investigators considered any death to be treatment-related if analytical analyses tested positive for chlorpyrifos residues in samples, as shown in the following table."

Field investigators classified casualties as either likely treatment related, may have been treatment related, could not be determined, or considered not treatment related. If a carcass contained an internal chlorpyrifos residue, it was classified as likely treatment related. If a carcass contained an external chlorpyrifos residue, such as on the feathers, skin or pelt, it was classified as may have been treatment related. This distinction is made because there can be cases where an external residue is unrelated to the cause of death. The most obvious example is the direct overspray of an old carcass.

The draft science chapter tabulates some Iowa cornfield data on page 55. Corrections and clarifications are given in **BOLDFACE**.

WILDLIFE OBSERVATIONS & DEATHS IN CHLORPYRIFOS-TREATED CORN								
Parameters	Reference Areas 1st/ 2nd/ 3rd/ 4th	Lorsban 4E Areas 1st/ 2nd/ 3rd/ 4th	Lorsban 15G Areas 1st / 2nd / 3rd					
# of Censuses	45/ 28/ 39/ 30	55/ 34/ 40/ 29	53/ 40/ 31					
# of bird species	60/ 49/ 50/ 43	67/ 51/ 53/ 41	61/ 48/ 41					
Total birds observed	1210/ 857/1257/1088	1369/1027/1276/949	1231/ 1156/ 987					
# of Species in corn	17/ 10/ 18/ 12	24/ 19/ 17/ 17	16/ 15/ 14					
# Observed in corn	110/ 50/ 64/ 51	100/ 97/ 63/ 81	52/ 67/ 65					
# of Post-treatment bird casualties	6/ 0/ 5/ 3	2/ 6/ 3/ 2	6/ 1/ 2					
Analyzed:positive ^a	0:0 / 0:0 / 1:0 / 1:0	0:0 / 0:0 / 0:0 / 1: 1 ^b	0:0/ 1:0°/ 0:0					
# of Post-treatment mammal casualties	3 / 6/ 1/ 0	2/ 3/ 3/ 1	0/ 4/ 3					
Analyzed:positive ^a	2 :0 / 4 :0 / 0:0 / 0:0	0: 0 / 1:0 / 1:0 / 1:1 ^d	0:0 / 0: 0 ^e / 2:1 ^f					
# of Post-treatment reptile casualties	2 / 2/ 0/ 0	3/ 1/ 0/ 0	0/ 0/ 0					
Analyzed:positive ^a	0:0 / 0:0 / 0:0 / 0:0	0:0 / 0:0 / 0:0 / 0:0	0/- / 0/- / 0/-					
# of Post-treatment amphibian casualties	0/ 0/ 1/ 0	0/ 0/ 0/ 1	0/ 0/ 1					
Analyzed:positive ^a	0:0 / 0:0 / 0:0 / 0:0	0:0 / 0:0 / 0:0 / 0:0	0/- / 0/- / 1/0					
Total # post- treatment casualties	29	27	17					
Analyzed:positive ^a	8:0	4:2	4:1					

The number of **post-treatment** carcasses analyzed for chlorpyrifos residues and number of carcasses found to contain chlorpyrifos.

Deleted footnotes g, h, and i as superfluous or inconsistent with table entries

Two robins were caught showing cholinesterase inhibition; one robin died with 5.8 ppm on skin, but negative for chlorpyrifos internally. The other bird recovered and was released unanalyzed.

A brown **thrasher** was hit by a car, analysis was negative for chlorpyrifos.

The carcass of a field mouse, *Peromyscus* sp. contained 0.7 ppm.

^e An eastern cottontail rabbit was found slightly affected (cholinesterase inhibition, but it could not be caught;.

A short-tailed shrew contained 2.1 ppm in its internal tissues; a second shrew exhibited behaviors typical of cholinesterase inhibition; but could not be captured and was therefore not analyzed.

The major corrections included in the above table are adding the counts of analyzed animals from the control fields and omitting live animals from counts of carcasses.

The draft science chapter states on page 56

Post-treatment casualties in Lorsban 4E, sprayed fields included 27 carcasses (i.e., 13 birds, 9 mammals, 4 snakes, and a northern leopard frog). Carcasses found in Lorsban 15G-treated fields included 17 casualties ...

The science chapter drops the necessary distinction between casualties and carcasses. Carcasses are dead animals, casualties are both dead animals and animals that are live but behaving abnormally, in a manner consistent with cholinesterase depression. To count all casualties as carcasses is incorrect. This should read, "...included 27 casualties...

The draft science chapter states on page 56

(i.e., 9 birds, 3 mammals and American toad).

This should read "(i.e., 9 birds, 7 mammals, and an American toad)".

The draft science chapter states on page 56

Only seven carcasses (9.6%) were analyzed for chlorpyrifos.

Sixteen (21.9%), not seven (9.6%), of the 73 casualties found post-treatment were analyzed for chlorpyrifos.

The draft science chapter states on page 56

Four carcasses were negative for chlorpyrifos, including a thrush, vole, shrew, and toad.

Eight post-treatment casualties from treated fields were in a condition suitable for residue analysis. Of these, five, not four, contained less than detectable chlorpyrifos. These five were a

brown thrasher, a meadow vole, a mole, a northern short-tailed shrew, and an American toad. These were samples 103-366-C150, -C113, -C205, -C149, and -C195, respectively.

The draft science chapter states on page 56

Consequently, out of ten animals for which possible chlorpyrifos effects were actually determined 40% were negative and 60% were positive for chlorpyrifos residues or cholinesterase inhibition.

Adding the count of abnormally behaving animals to those dead animals that gave detectable chlorpyrifos residues incorrectly inflates the calculated percentage of adversely affected animals. If counts of abnormally behaving animals are included in the numerator, then the counts of those animals that were seen without abnormal behavior should be included in the denominator. A corrected version would read: "About one-third of the carcasses (3 of 8, or 37.5%) collected post-treatment from treated areas and in a condition suitable for residue analysis contained detectable chlorpyrifos." It should be noted that seven additional animal casualties, not counted above, were collected from invertebrate pit traps. These traps were installed on treated areas immediately after treatment. They were visited within 24 hours and periodically thereafter. Six of the seven casualties collected were intact carcasses suitable for analysis; one of these contained a detectable residue. Adding the totals from the pit traps the statement would be corrected to read: "Less than one-third of the carcasses (4 of 14, or 29%) collected post-treatment from treated areas and in a condition suitable for residue analysis contained detectable chlorpyrifos."

If counts of abnormally behaving animals are to be considered, the statement should read something like: "Of the more than 11,000 bird observations in the Iowa corn study, including the 337 bird observations made in the several hours immediately following the application of chlorpyrifos, only four birds were observed behaving abnormally." A similar statement could be made for the other animals observed.

The draft science chapter states on page 56

"The supplementary corn field study provides useful information, which generally support the

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residue levels and avian and mammalian mortality predicted in the above risk assessment (Frey

et al. 1994, MRID 43483101)."

The measured residues for non-target avian and mammalian food items, particularly insects, are

much lower than those predicted.

The draft science chapter states on page 111

"Although, many dead animals were found, residue analysis was performed on only 9 birds and

small mammals. Five animals (56 percent) tested positive for chlorpyrifos residues and one

rabbit was found showing signs of cholinesterase inhibition, but it escaped capture."

For the Iowa corn study, 34 of 114 casualties were carcasses in a condition suitable for residue

analysis and were analyzed. If only post-treatment casualties from treated areas are counted, the

counts are reduced to eight suitable and analyzed out of 44 casualties for the Iowa corn study; of

these, three (37.5%), not five, contained a detectable chlorpyrifos residue.

The draft science chapter states on page 127

Seventeen carcasses were found on the granular-treated fields. Only three carcasses were

analyzed for chlorpyrifos.

Four, not three, of 17 casualties were carcasses in a condition suitable for analysis; all four were

analyzed.

The draft science chapter states on page 127

A brown thrush was hit by a car, analyzed and found negative for chlorpyrifos.

This was a brown thrasher.

The draft science chapter states on page 127

Three out of four animals, 75 percent, either tested positive for chlorpyrifos or showed behavior

indicative of cholinesterase inhibition."

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Of the post-treatment casualties from granular treated fields, four were carcasses in a condition suitable for analysis and only one of these contained a chlorpyrifos residue.

The draft science chapter states on page 131

If the percentage of casualties testing positive for chlorpyrifos residues reflect the percentage of all casualties found, approximately 60 percent of the casualties are affected by chlorpyrifos. If the 60 percent, chlorpyrifos-affected wildlife is extrapolated to the total local population and corrected for percent recovery and percent of treated area, covered in carcass searches, the estimate of number of wildlife affected by chlorpyrifos should begin to raise concerns about non-target species.

About 30%, not 60%, of the carcasses that could be analyzed and that were collected post-treatment from treated areas contained a detectable chlorpyrifos residue.

F.2.1.3 California Citrus (Orange Grove) Study

The draft science chapter tabulates some California citrus data on pages 56-57. Corrections and clarifications are given in **BOLDFACE**.

WILDLIFE OBSERVATIONS & DEATHS IN CHLORPYRIFOS-TREATED CITRUS					
Parameters	Reference Areas 1st / 2nd	Treatment A Areas 1st / 2nd	Treatment B Areas 1st / 2nd		
# of Censuses	28 / 37	30 / 38	20 / 45		
# of bird species	44 / 49	48 / 33	42 / 47		
Total birds observed	708 / 1,182	893 / 1,101	543 / 1,425		
Birds observed in groves	201 / 399	309 / 403	188 / 561		
# of post-treatment bird casualties	35 / 16	27 / 16	17 / 11		
Analyzed/positive	4/0 1/0	3/0 / 2/1 ^a	2/0 / 1/1 ^d		
# of post-treatment mammals casualties	10 / 8	11 / 10	10 / 4		
Analyzed/positive	3/0 2/0	4/0 / 4/ 0 ^b	3/1 ^e / 0/-		
# of post-treatment reptiles casualties	2 / 3	1 / 2	2 / 0		
Analyzed/positive	1/0 1/0	0/- / 1/1°	1/0 / 0/-		
# of post-treatment amphibia casualties	2 / 0	1 / 3	1 / 0		
Analyzed/positive	0/- / 0/-	0/- / 0/-	0/- / 0/-		
Total # post-treatment casualties	49 / 27	40 / 31	30 / 15		
Analyzed/positive	8/0 4/0	7/0 / 7/2	6/1 / 1/1		

Page 57, footnote b under the table: "No chlorpyrifos detected in carcasses of ground squirrel and pocket gopher, but 1.53 ppm and 1.51 ppm was on the pelts, respectively, indicating the death may have been treatment related. It should be noted that all four analyzable mammal carcasses were found on Replicate A1 where the grove manager had put out mammal poisons prior to these collections."

Since the only four analyzable mammals were found on the same site and none of them had detectable internal chlorpyrifos residues, and due to the relatively low mammalian toxicity of chlorpyrifos, the evidence strongly suggests that the ground squirrel and pocket gopher died from mammal poison and not from chlorpyrifos exposure. The table should be changed accordingly.

Page 57, last paragraph ending on page 58: "Out of the 192 casualties found on all citrus replicates only 21 carcasses were analyzed for the presence of chlorpyrifos. Six of the 21 carcasses (28.6 %) were found to have chlorpyrifos residues either in the carcass or on the pelt and consequently assume that they may have died from treatments. Species that tested positive for chlorpyrifos were a mockingbird, an unidentified passerine nestling, house mouse, ground squirrel, pocket gopher, and a western rattle snake. While the number of dead wildlife found during carcass searches does not show a dose-relationship with treatment levels, the number of carcasses testing positive for chlorpyrifos does (i.e., 4 carcasses at 6 lbs ai/A, 1 each at 3.5 and 4 lbs ai/A, and none at 1.5 lbs ai/A, but the number of positive carcasses are too few to verify this conclusion. These results should not be used to conclude to that 1.5 lbs ai/A does not kill wildlife. Carcasses found on reference replicates were not analyzed for the cause of death, because the authors assumed that all reference deaths represent natural deaths. According to the report, carcasses found during other activities were added to those found during carcass searches. Since most extra time was spent on reference groves evaluating other monitoring methods, the number of carcasses represent inflated numbers of death on reference plots."

The first sentence sounds like someone was trying to avoid analyzing all the analyzable samples. The sentence should read, "Out of 192 post-treatment casualties found on all citrus replicates only 33 carcasses **could be** analyzed for the presence of chlorpyrifos."

The second sentence needs to be changed to, "Four of the 33 carcasses (12.1%) may have died

The third sentence should be changed to, "Species that tested positive for chlorpyrifos and were not potentially baited and poisoned were a mockingbird, an unidentified passerine nestling, house mouse, and a western rattle snake."

The sixth sentence should be deleted: "Carcasses found on reference replicates were not analyzed for the cause of death, because the authors assumed that all reference deaths represent natural deaths." The control carcasses were analyzed for chlorpyrifos residues (see Table 4 of Gallagher et al., 1994).

There needs to be a sentence added to the end of this paragraph. For example, "When casualties found outside the casualty searches are removed and the data are reanalyzed, the conclusion is the same: There is no treatment-related increase in casualties." (See next comment below.)

Page 58, 2nd paragraph, last sentence: "The citrus field study provides useful information, but it would not support a registration requirement for chlorpyrifos use on citrus, because the casualties reported for untreated orchards resulted from unequal (greater) search time on the untreated orchards and control carcasses were not analyzed for chlorpyrifos residues (Gallagher et al., 1994, MRID 437303-01, 437067-01)."

The statistical analysis provided by Fontaine (1995a) demonstrates that when casualties found outside the casualty searches are removed and the data are reanalyzed, the conclusion is the same: there is no treatment-related increase in casualties. Furthermore, control carcasses that could be analyzed for chlorpyrifos (see Table 4 of Gallagher et al., 1994) were analyzed, but there were no detectable residues. Therefore, this study should support a registration requirement for chlorpyrifos use on citrus.

F.2.1.4 Florida Turf (Golf Course) Study

The draft science chapter states on pages 59-60. Corrections and clarifications are given in **BOLDFACE.**

WILDLIFE OBSERVATIONS AND DEATHS ON CHLORPYRIFOS-TREATED TURF					
Parameters	Reference Areas	Liquid-treated Areas	Granular-treated Areas		
# of Censuses	60 (12/rep.)	63 (12.75/rep.)	63 (12.75 /rep.)		
# of bird species	66	68	63		
Total birds observed	1,755	2,059	2,336		
Birds observed on turf	391	763	345		
# of post-treatment bird casualties	3	4	2		
Analyzed/positive	1 / 0	1 / 0 ^a	0 / -		
# of post-treatment mammal casualties	1	1	0		
Analyzed/positive	0 / -	0 / -	-/-		
# of post-treatment reptile casualties	0	4	3		
Analyzed/positive	-/-	3 / 1 ^b	2 / 1		
# of post-treatment Amphibia casualties	0	2	6		
Analyzed/positive	-/-	2/0°	1/0		
Total # post-treatment casualties	4	11	11		
Analyzed/positive	1 / 0	6/1	3 / 1		

Double-crested cormorant showed cholinesterase behavior, but was negative for chlorpyrifos. **Multiple** acephate treatments subsequent to chlorpyrifos treatment with one acephate treatment occurring the day prior to the observation of the cormorant, strongly suggests that chlorpyrifos was not the proximate cause of this observation.

The major corrections included in the above table are adding the counts of analyzed animals from the control fields and omitting live animals from counts of carcasses.

The draft science chapter states on page 60.

b Florida soft-shell turtle positive casualty based on residues of 1.09 ppm.

^c Southern toad showed cholinesterase behavior, but was < 0.5 ppm chlorpyrifos

"The turf-treated golf course field study provides useful information, but it would not support a registration requirement for chlorpyrifos use on turf, because the casualties reported from untreated golf courses resulted from unequal (greater) search time on untreated golf courses and control carcasses were not analyzed for chlorpyrifos residues (Worley et al. 1994, MRID 437852-01, 437852-02)."

Analysis of the casualty data presented in Fontaine (1995b) uses the casualty counts obtained during scheduled casualty searches. Since these are of equal intensity on treated and control courses there can be no effect attributable to unequal search intensity. The result from this analysis was that there was no statistical evidence for excess mortality on treated courses.

Although there was only one control carcass in a condition suitable for residue analysis, sample 103-364-C90, it was analyzed and it contained no detectable chlorpyrifos.

The draft science chapter states on page 61

"Results from terrestrial field studies in total indicate chlorpyrifos-related mortality for some species in every Class of vertebrates, including birds, small mammals, snakes, aquatic turtle, toad, and fish)."

No toad from the three terrestrial field studies (Iowa corn, California citrus, Florida turf) contained detectable chlorpyrifos.

No examples of some classes of vertebrates, e.g., agnatha, crossopterygii, were found in the three field studies.

The draft science chapter states on page 61

"In the three major field studies, few carcasses of those found were analyzed for chlorpyrifos residues (i.e., 7 out of 44 animals in the corn study, 21 out of 116 in the citrus study, and 5 out of 22 golf course turf studies)."

Carcasses that were found in a condition suitable for residue analysis were analyzed. For the Iowa corn study, 34 of 114 casualties were carcasses in a condition suitable for residue analysis and were analyzed. For the Florida turf study, 12 of 34 casualties were carcasses in a condition

suitable for residue analysis and were analyzed. For the California citrus study, 40 of 220 casualties were carcasses in a condition suitable for residue analysis and were analyzed. If only post-treatment casualties from treated areas are counted, the counts are reduced to eight suitable and analyzed out of 44 casualties for the Iowa corn study, 21 suitable and analyzed out of 116 for the California citrus study, and nine suitable and analyzed out of 22 for the Florida turf study.

The draft science chapter states on page 61

"None of the carcasses from control areas were analyzed for chlorpyrifos or other causes of

Carcasses found in a condition suitable for residue analysis were analyzed regardless of whether they were collected from control or treated areas. Twenty-one animals collected from the control areas during the post-treatment time period in the three field studies were analyzed for chlorpyrifos. None contained a detectable chlorpyrifos residue.

The draft science chapter states on page 96

"Three extensive terrestrial field studies on corn in Iowa, citrus in California, and golf courses in central Florida, report cholinesterase-inhibition effects and chlorpyrifos-related mortality in non-target organisms. Chlorpyrifos-related mortalities were reported in small mammals, birds, snakes, an aquatic turtle, and amphibians as determined by measurable chlorpyrifos residues in the carcasses."

No amphibians collected in the three terrestrial field studies contained detectable chlorpyrifos.

F.2.2 Uncited Studies

The last two paragraphs on page 60 (finishing on the top of page 61), describes two supplemental reports on terrestrial field studies that report the effects of chlorpyrifos on mammals and birds (Kenega, 1968; Clements and Bale, 1988). Below are additional reports of field studies that examined the effects of chlorpyrifos on terrestrial wildlife. These papers could also be used to show that for every report of terrestrial field incident (see pp 61-63), there is a field study that

shows few or no incidents. This is important when using a "weight of the evidence" approach for risk assessment.

A study using radio-tagged great horned owls, which consume small mammals that could contain insecticide residues, demonstrated anti-cholinesterase exposure, but no effects, following insecticidal treatment of Iowa corn fields (Buck et al., 1996). Seven owls were monitored in 1988 and 15 owls were monitored in 1989, both before and after treatment of corn fields in south central Iowa with terbufos or chlorpyrifos (Lorsban 15G granular insecticide). Plasma butyrylcholinesterase activities from three owls captured post-application in 1989 were more than two standard deviations less than the control mean, indicating exposure to a cholinesterase-inhibiting insecticide. Differentiation between terbufos and chlorpyrifos exposure was not possible. The authors concluded that OP pesticide exposure occurs infrequently and at low levels in great horned owls.

A grassland study by Clements and Bale (1988) was cited in EFED science chapter. Another grassland study by Clements et al. (1992) confirmed exposure and no apparent effects in geese feeding on two grassland sites in England (Apuldram, ca. 15 ha and Hurst ca. 10 ha) treated with a liquid formulation of chlorpyrifos at 0.72 kg a.i./ ha. At the Apuldram site a flock of from 111 to 500 Brant per day arrived between 8:15 and 9:20 AM each day and grazed more or less continuously until about 4:00 PM to 5:00 PM. Observations of the number of geese and their behavior were made on two occasions before spraying and four occasions after. Observations enabled an activity index and a count of pecks/minute to be calculated. No changes in the numbers or behavior of the geese that could be attributed to chlorpyrifos application were found. Thorough searches were made for cadavers on the experimental fields, their environs and the roosts on three occasions before spraying and five occasions after (2, 6, 15, 27, and 36 days after treatment). No carcasses were found apart from one dead sheep that had climbed into a metal water tank (0.8 m high) and apparently drowned. Analysis of grass and goose feces confirmed that geese were exposed to chlorpyrifos at the site. Maximum grass residue was 20 ppm and the maximum feces residue was 10 ppm. The Hurst site was used by a flock of from 46 to 323 Canada geese per day. Observations of the number of geese and their behavior were made on

three occasions before spraying and four occasions after. No changes in the numbers or behavior of the geese that could be attributed to chlorpyrifos application were found. Thorough searches were made for carcasses on the experimental fields, their environs and the roosts on two occasions before spraying and four occasions after (2, 9, 23, and 37 days after treatment). Only one carcass was found. This goose, however, was not subjected to a post-mortem examination but had clearly died from being entwined in and swallowing some fishing equipment. Analysis of grass and goose feces confirmed that geese were exposed to chlorpyrifos at the site. Maximum grass residue was 20 ppm and the maximum feces residue was 4 ppm. The authors concluded that "chlorpyrifos application to pasture had no perceptible or statistically significant effect on

Lorsban 4E treatment of 16 contiguous ha (0.56 kg a.i./ha, aerial application) and two 4-ha swaths (1.0 kg a.i./ha, aerial application) of winter wheat in Montana was made to control pale western cutworms in late May, 1982 (McEwen et al., 1986). Horned larks and McCain's long spurs, feeding on the treated fields, had a very high proportion (50 and 70%, respectively) of Lepidoptera, mostly pale western cutworms, the target pest, in their stomachs when first collected at three days post-treatment. Brain ChE activity of 16 horned larks collected on day 3 averaged 22% depressed below reference levels of birds collected from unsprayed rangeland. Eighteen horned larks collected on day 9 averaged 18% depression. By day 16, 20 horned larks averaged 8% depression, an amount statistically indistinguishable from the control at p<0.05. The 11 McCain's long spurs collected on days 3 and 9 after treatment had brain ChE activities statistically indistinguishable from those of the controls. No sick or dying birds were observed at any time though no systematic searches or censuses were conducted. Two of the 34 horned larks, collected on 3 and 9 days after treatment, had brain ChE levels inhibited 44 and 52%, respectively. The authors concluded that "chlorpyrifos did not appear to have a severe direct

Two 600-ha plots in northern Senegal were treated aerially with a liquid chlorpyrifos formulation at 0.27 and 0.387 kg a.i./ha to control grasshoppers (Mullié and Keith, 1993). Similar to the findings of McEwen et al. (1986; see full reference above) local birds, singing bush larks,

Abyssinian rollers, and buffalo weavers, consumed the target pest as a major component of their diet. Adult bush larks collected one week after application on the 0.27 kg/ha plot had 14% depression of brain ChE (n = 7) while two bush larks collected from the higher rate plot (0.387 kg/ha) averaged 17% depression. Neither of these group means was two standard deviations less than the control mean and individual activities were not given, so the number of individuals falling below the two standard deviation level could not be calculated. Bush larks (n = 4) collected three weeks post-treatment had average brain ChE activity greater than the controls. Insufficient numbers of other live collected birds made comparisons of other species exposure and effects impractical. Flightless bush lark fledglings collected live on the ground on both treated fields at 24 and 48 hour post application had mean brain ChE activities 33 - 45% below the single fledgling control activity level. Flightless bush lark fledglings from chlorpyrifos-treated sites were significantly lighter (8.2% lighter) than their similarly-aged counterparts from control sites. Four dead birds and one debilitated bird were collected on the chlorpyrifos plot treated at the higher 0.387 kg/ha rate. One additional debilitated bird was collected from the chlorpyrifos plot treated at the lower rate. No dead or debilitated birds were collected during identical searches of the control plot. Three of the four dead birds were Abyssinian rollers and their gizzards contained 32, 29, and 51 grasshoppers. Rollers collected live from control and treated fields had only 14 to 19 grasshoppers per gizzard, suggesting that a shift to feeding on abundant and easily available dying grasshoppers may have led to rapid intoxication and death. Brain ChE depression was 40% and 52% for the two dead Abyssinian rollers for which it was measured, though only the latter of the two birds' brain ChE activities fell below the two standard deviation measure. These results are consistent with those obtained in the Montana wheat fields; a fraction of those birds that are aggressively feeding on the target pest shortly after treatment can experience ChE inhibition. In Senegal, where the size of the treated area, 600 ha, suggests the birds were feeding exclusively on treated substrates, some affected birds died and were discovered. The number of dead or debilitated birds, 5 and 1, correspond to casualty rates of 0.05 casualties/ha searched and 0.01 casualties/ha searched, on the 0.387 kg/ha and 0.27 kg/ha treatments, respectively.

F.2.2.1 Large Pen, Simulated Field Study

Not applicable.

F.2.2.2 Iowa Corn Study

The statistical review of the Iowa corn casualty and observation data (Fontaine, 1994) is not cited. This study examines the casualty data obtained from carcass search transects. These searches were performed with equal intensity on treated and untreated fields. There were no statistically significant differences between the avian casualty counts on treated and untreated fields.

F.2.2.3 California Citrus (Orange Grove) Study

A statistical review of this study by Fontaine (1995a) is not referenced. The report is important for the following reasons: (1) It refutes the presumption that, "Measured residue levels reported in field studies on corn, citrus and golf courses sprayed with chlorpyrifos support the use of maximum residue levels for risk assessment." (See p 16 under Non-granular Exposures and Assumptions.); (2) It normalizes the data for carcass searches (if anything, it errs on the conservative side, i.e., biases the data toward too few casualties found on the reference sites) and still shows that "the casualty data provide no evidence for a significant treatment-related increase in casualties for either all animals or all birds."; and, (3) It emphasizes the fact that the mean residues measured immediately after application in soil, citrus foliage, adjacent vegetation, water, and invertebrates are lower than the EECs used by EFED and that they decline monotypically with half-lives less than two weeks. It also highlights an important point: day of application residues from invertebrates (a major food source for birds during the breeding season) are 10 times less than the EECs used by EFED. Chlorpyrifos residues from invertebrate samples were reduced to less than half their initial value seven days post-treatment. This is very important in a weight-of-the-evidence analysis.

F.2.2.4 Florida Turf (Golf Course) Study

The statistical review of the Florida turf casualty and observation data (Fontaine, 1995b) is not cited. This study examines the casualty data obtained from carcass search transects. These searches were performed with equal intensity on treated and untreated fields. There were no statistically significant differences between the avian casualty counts on treated and untreated turf.

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F.2.3 Omission of Other Relevant Data

Not applicable.

F.2.4 Differences in Interpretation of Evidence

F.2.4.1 Large Pen, Simulated Field Study

EFED reports that the LOEL was based on abnormal behavior and mortality. This is misrepresentation of the conclusions. The LOEL is only based on abnormal behavior.

On page 16 under Non-Granular Exposures and Assumptions, "Measured residue levels reported in field studies on corn, citrus and golf courses sprayed with chlorpyrifos support the use of maximum residue levels for risk assessment." This is a misrepresentation of the data and excludes the results of the pen study summarized by EFED. "The mean measured, initial chlorpyrifos levels from 3 + 3 and 6 lbs ai/A treatments were reported as 306 and 903 ppm on grass and 12 and 30 ppm on seeds, respectively. These residue levels are about half of the chlorpyrifos EECs (720 and 1440 ppm for turf and 45 and 90 ppm for seeds)."

F.2.4.2 Iowa Corn Study

The draft science chapter states on page 56

Another three animals (a robin, rabbit, and shrew) were determined to be chlorpyrifos casualties based on behaviors typical of cholinesterase inhibition.

These casualties were classified as may have been treatment related, not determined, and may have been treatment related. Since researchers were unable to capture the rabbit or the shrew no chemical analysis was possible. The robin was captured, it recovered and was released with no analysis having been performed. To conclude that these casualties were caused by chlorpyrifos is an unwarranted extension of the data.

The draft science chapter states on page 110

"Wildlife utilization of corn fields is high with a broad diversity of avian and mammalian species. Wildlife reported to feed moderately to high in corn fields include quail, grouse,

partridge, pheasant, prairie chicken, ducks, doves, songbirds (35 species), red fox, muskrat, opossum, raccoon, and deer to a low to high degree. While it is unlikely that deer might be adversely affected, because of their large size, many of the other species could be affected by consumption of food items (such as seeds, insects and vegetation) found in chlorpyrifos-treated cotton fields. Bobwhite quail, pheasant (brood-rearing), and rabbits also nest and brood young in corn fields. In the Iowa corn field study, the number of avian species observed in corn field in various replicates ranged from 12 to 24 species in six circular plots per field. The number of individual birds seen in corn replicates ranged from 50 to 110 birds. The number of birds observed in corn fields total 768 birds in the circular plots."

This is an inaccurate oversimplification. No animal has evolved so that corn monoculture provides its preferred habitat. It is not surprising that edge and less disturbed areas usually provide the most widely used habitat. For example, of the over 11000 bird observations, 768 were in the corn fields. It would be more accurate to say that the vast majority of bird observations were not in the corn fields. In addition, wildlife utilization of corn fields varied dramatically over the course of a season as the field went from bare ground to mature corn. The reference to chlorpyrifos-treated cotton fields should be corrected.

F.2.4.3 California Citrus (Orange Grove) Study

Page 57, footnote b under the table: "No chlorpyrifos detected in carcasses of ground squirrel and pocket gopher, but 1.53 ppm and 1.51 ppm was on the pelts, respectively, indicating the death may have been treatment related. It should be noted that all four analyzable mammal carcasses were found on Replicate A1 where the grove manager had put out mammal poisons prior to these collections."

Since the only four analyzable mammals were found on the same site and none of them had detectable internal chlorpyrifos residues, and due to the relatively low mammalian toxicity of chlorpyrifos, the evidence strongly suggests that the ground squirrel and pocket gopher died from mammal poison and not from chlorpyrifos exposure. The numbers in the table should be changed accordingly (see table in the **Errors** section under <u>California Citrus (Orange Grove) Study</u> above).

F.2.4.4 Florida Turf (Golf Course) Study

The draft science chapter states on page 61

"Out of the 33 carcasses tested for chlorpyrifos, 3 out of 7 carcasses tested positive and a robin, shrew, and rabbit were reported to show behavior indicative of cholinesterase inhibition in the

corn study; in the citrus study, 3 carcasses and 3 pelts tested positive out of 21 carcasses analyzed; and in the golf course turf study, 2 out of 5 carcasses tested positive and a double-crested cormorant and southern toad showed cholinesterase behavior."

The implication is that all animals displaying cholinesterase behavior should be counted as adverse effects from chlorpyrifos exposure. There are several examples suggesting that this is not likely. One of the two abnormal animals was a southern toad whose whole carcass, when analyzed, contained less than the detection limit (0.5 ppm) as chlorpyrifos. Counting this animal as positive for chlorpyrifos effects is not warranted by the data. The second abnormal animal, a double-crested cormorant, was captured on study area L4, on September 12, 1992, 22 days after that area was treated with chlorpyrifos (4.5 kg/ha). That area was treated five times with acephate (3.4 kg a.i./ha), on 1, 9, 15, 19, and 23 days prior the collection of the bird. Acephate is a cholinesterase inhibiting insecticide that has methamidophos, another cholinesterase inhibitor, as a degradation product (Pesticide Manual, 1995). The toxicities of methamidophos, chlorpyrifos, and acephate to the mallard are 30 (Pesticide Manual, 1995), 75 (Schafer, et. al., 1983), and 350 mg/kg (Pesticide Manual, 1995), respectively. The cormorant subsequently died. Analyses of the skin and feathers, and the remainder of the bird, yielded no detectable chlorpyrifos. It is unlikely that this bird was affected by the chlorpyrifos application 22 days prior to its capture.

The draft science chapter states on page 61

"Low carcass recovery rates reported in some chlorpyrifos fields studies and the relatively small search areas to total area treated suggest that the number of reported carcasses may grossly underestimate the number of non-target wildlife adversely affected by chlorpyrifos uses on these sites."

Low carcass recovery rates and a small ratio of area searched to area treated would suggest that the ratio of unrecovered carcasses to recovered carcasses is large. This says nothing whatsoever about whether these carcasses might be due to chlorpyrifos treatment or some other cause. It is of greater interest to determine whether there has been sufficient recovery of casualties to allow a comparison of casualty rates on treated and controls. The three field studies provide no statistical evidence for a greater casualty rate on the treated areas.

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The draft science chapter states on page 61

"Based on the time to death in the acute oral studies, affected non-target wildlife would have ample time to move far offsite or hide in the field and adjacent habitats before dying."

Since neither time to death nor the time evolution of the symptoms of exposure is presented in the science chapter, this speculation about the behavior of potentially exposed animals is entirely unsupported by data.

The draft science chapter states on page 98

"Results from the three terrestrial field studies on corn, citrus and golf courses and several incidents with robins and other bird species reported for lawn and residential perimeter treatments associated with termiticide uses, support risk quotient assessments of risks to both birds and reptiles from chlorpyrifos uses".

The casualty data from the terrestrial fields studies demonstrate that the mortality risks to nontarget terrestrial animals on chlorpyrifos treated fields are not statistically distinguished from those on untreated fields.

The draft science chapter states on page 99

"Chlorpyrifos-treated fields are unlikely to produce the large visible bird kills, like those reported for carbofuran and some other fast-acting insecticides, which is not to say that many birds are not killed by chlorpyrifos. In the chlorpyrifos acute oral tests, the onset of avian symptoms predominately occurred between 20 minutes and 4 hours after dosing and deaths occurred within 24 hours. Thus, birds have adequate time to feed in chlorpyrifos-treated fields, leave the treated area and disperse to other habitats before they begin to experience toxic symptoms, then they seek refuge and hide before dying."

In acute oral tests birds are caged. Whether those birds that consume a lethal dose could leave a treated field is unknown. The scenario that has birds consuming fatal doses of chlorpyrifos, leaving the treated area prior to experiencing toxic symptoms is pure speculation and utterly unsupported by data. It is another example of arguing from a preconceived conclusion to a scenario that supports that conclusion. An alternative explanation for the low numbers of good intact bird carcasses, and one that is consistent with the lack of significant difference between

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treated and untreated casualty counts, is that chlorpyrifos is not responsible for a significant number of bird deaths.

F.3 Terrestrial Incident Reports

- 1. Page 61, 2nd line from the bottom states: "According to Huang et al. (1994), the toxicity of diazinon and chlorpyrifos are considered additive, at least in aquatic tests." This sentence and reference should be removed for the following reasons: (1) The Huang et al. reference is an unpublished abstract. The work has not been validated. (2) The work was done with one aquatic organism (mysids); no terrestrial animals were tested. (3) Huang et al. state that, "A mixture of chlorpyrifos, diazinon, and methidathion produced additive toxicity to mysids." There is no mention of additive toxicity to terrestrial wildlife with chlorpyrifos and diazinon or chlorpyrifos and carbofuran alone (see point 3 below).
- 2. Page 62, 1st paragraph, last sentence: "In the three field studies, researchers assumed that if chlorpyrifos residues were present, then the animal had been affected by chlorpyrifos." This is a misrepresentation of the conclusions. Each animal was examined on a case-by-case basis. Based upon the results of residue analyses and the circumstances under which the casualties were found, each casualty was classified either as likely treatment related, may have been treatment related, could not be determined, or considered not treatment related. The criteria for each classification were detailed in each report.
- 3. Page 62, 1st 4 full paragraphs: The first three paragraphs are incident reports of geese killed after applications of chlorpyrifos and diazinon. The fourth paragraph is an incident involving six waterfowl where chlorpyrifos and carbofuran are identified as present. It cannot be proved that chlorpyrifos did not contribute to the deaths of those birds. However, both diazinon and carbofuran are more toxic to birds (especially waterfowl) relative to chlorpyrifos (Hill and Camardese, 1984; Hudson et al., 1984). The inference from the first paragraph in this section that the combination of chlorpyrifos and diazinon cause additive toxicity is unfounded. There is no conclusive evidence for this presumption (see point #1 above).

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4. Page 62, 3rd full paragraph: These incidents were cited in Smith (1987) but reported in Hazard Evaluation Division (1981).

- 5. Page 62, last paragraph, last sentence: This sentence is misleading; it should be deleted or moved to the next paragraph.
- 6. Pages 62-63: The last five incident reports have no references.
- 7. Chlorpyrifos is classified as toxic to some birds and mammals. Therefore, it is not surprising that there are occasional reports of terrestrial incidents. It should be noted, however, that after more than three decades of chlorpyrifos use and numerous applications, relatively few non-target, terrestrial wildlife incidents have occurred. In a weight-of-the-evidence analysis, chlorpyrifos clearly does not cause the magnitude of mortality predicted by EFED screening level assessments.

Appendix G: Refinement of Risk Quotients

G.1 Toxicity Corrections

G.1.1 Terrestrial Toxicity Corrections, Lorsban 15G Granular Insecticide

Toxicity to mammals is based on the toxicity of Lorsban 15G to the female rat. Other mammals are assumed to have the same sensitivity in terms of mg/kg as the rat. Toxicity values are scaled to reflect body size. The bird data is the sparrow data (lowest valid LD_{50} value).

G.1.2 Corrected Table from Pages 19-20 of the Draft Science Chapter:

Granular Risks to Wildlife Expressed as Number of Granules per LD_{50.} Toxicity to untested birds assumed to be equivalent to the most sensitive species tested, the rock dove; while mammals are assumed to be as sensitive as female rats. Species tested with granular formulations are in bold. (Lorsban 15 G average weight is 0.064 mg/granule and contains 0.0096 mg ai chlorpyrifos per granule)

formulations are in bold . (Lorsban 1	formulations are in bold. (Lorsban 15 G average weight is 0.064 mg/granule and contains 0.0096 mg ai chlorpyrifos per granule)					
Species	LD ₅₀ (mg a.i /kg body wt.)	Body Weight (kg)	mg/LD ₅₀	Granules/LD ₅₀		
House Sparrow Passer domesticus (MRID 44057101)	111	0.025	2.77	289		
Rock Dove ^A Columba livia (MRID 00045891)	54	0.350	18.9	1,969		
Ringe Turtledove ^A Streptopelia risoria Hill & Camardese, 1984	157	0.150	23.5	2,448		
Bobwhite Quail Colinus virginianus Hill & Camardese, 1984, Cited by Smith, 1987 MRID41043901)	108	0.200	21.6	2,250		
Rat (Female) Rattus norvegicus (MRID 44248604)	193	0.124	23.9	2,490		
Rat (Male) Rattus norvegicus (MRID 44248604)	337	0.170	57.3	5969		
Common Grackle Quiscalus quiscula	54	0.114	6.2	645		
Red-winged Blackbird Agelaius phoeniceus	54	0.0526	2.8	292		
Mammal (15 grams body wt.)	193*	0.015	2.9	302		
Japanese Quail Coturnix japonica	54	0.178	9.6	1000		
Mammal (35 grams body wt.)	193	0.035	6.8	716		
Starling Sturnus vulgaris	54	0.0823	4.4	458		
Ring-necked Pheasant Phasianus colchicus	54	1.135	61.2	6,375		
Rat Rattus norvegicus	193	0.200	48.2	5,021		
Mallard Duck Anas platyrhynchos	54	1.082	58.4	6,083		
Mammal (1000 grams body wt.)	193	1.000	193	20,104		

^AThese studies were included as an example of granular toxicity recognizing that the number of birds used during the test (five for the rock dove and eight for the ringed turtledove) was too few to meet guideline requirements. However, they contribute to the weight of the science on the toxicity of granular chlorpyrifos to birds.

G.1.3 Terrestrial Toxicity Corrections, Lorsban* and Dursban* 4E Insecticide

G.1.3.1 Correction of Mammalian Toxicity Values, Pages 103-104 of the Draft Science Chapter

Assessment of risks to small mammals exposed to residues on food items requires the acute dietary LC_{50} value be converted mg/kg/day to estimate daily exposure. The geometric mean of the five valid rodent LC_{50} value 2027 ppm (p 51) was used as the reference LC_{50} value. To estimated daily LC_{50} concentrations for a variety of small to medium-sized mammals having different dietary needs, it is assumed that each species has the same sensitivity as the laboratory rat (e.g., LC50 = 2027 ppm). The laboratory rat was assumed to weigh 150 g and consume 10% of its body weight day⁻¹. The following formula was used to calculate the unknown LC_{50} values in mg/kg/day (Urban and Cook, 1986).

 $LC_{50}(mg/kg/day)_{untested\ species} = \underline{LC}_{50}\ (mg/kg)\ tested\ species\ x\ food\ consumed\ as\ \%\ body\ wt\ day^{-1}\ tested\ species$ food consumed as % body weight day^-1 untested species

The following table provides mammalian LC₅₀ values to be used in subsequent risk assessments.

Estimated LC_{50} values based on a reference rodent LC_{50} of 2027 ppm. Assuming untested species have the same sensitivity as the laboratory rodent and that the laboratory rodent weighs 0.150 kg and consumes 10% of its body weight day⁻¹

Mammalian Species	Body Weight (g)	% Body Wt Consumed per day	Est. 1-day LC ₅₀ ppm
Herbivores/Insectivores	15	95	213
	35	66	307
	1000	15	1,351
Granivores	15	21	965
	35	15	1,351
	1000	3	6,757

The avian acute dietary value is the geometric mean of the three core studies reported in the table on pages 45-46 of the draft science chapter. The mallard is the most sensitive species with three

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toxicity values. The geometric mean represents a conservative estimate of the true sensitivity of this species.

G.1.4 Aquatic Toxicity Corrections, Formulation Independent

Values are taken from Appendix E, Appendix Table E(4), duplicated below.

Appendix Table E(4). Revised acute and chronic toxicity effect concentrations for freshwater and saltwater organisms.

Test Description	Toxicity Effect Concentration (ug/L or ppb)		
Freshwater Fish Acute LC ₅₀	3.4		
Freshwater Fish Reproduction NOEC	0.57		
Freshwater Invertebrate Acute LC ₅₀	0.55		
Freshwater Invertebrate Reproduction NOEC	0.061		
Estuarine Fish Acute LC ₅₀	1.3		
Estuarine Fish Reproduction NOEC	0.28		
Estuarine Invertebrate Acute LC ₅₀	0.043		
Estuarine Invertebrate Reproduction NOEC	0.003		

G.2 Field Corn Lorsban 15G Granular Insecticide Example

G.2.1 Terrestrial Exposure Corrections

Corn Typical (banded 1.2 oz/1000 ft of row) scenarios (same for both MS and IA scenarios) broadcast basis for comparison to pages 128-130 tables (EPA value 1.7 mg/ft²)

surrogate	Exposure values
species	(mg/ft^2)
Mammalian	1.3
Acute	
Avian Acute	1.3

Assumptions: 1.2 oz a.i./1000 ft row, 9.2% exposed and 25% of the field area is bands (see Appendix D.2.4 and Appendix B). (Note 1.2 oz a.i./1000ft is a bit larger than 1.1 lb/A, actually about 1.3 lb/A).

$$mg \ ai \ / \ ft^2 = \frac{\left(12 \ oz \ / \ 1000 \ ft \ row\right) \ X28349 \ mg \ / \ oz \ X25\% \ fi \ el \ d \ ar \ ea \ i \ n \ bands \ X92\% \ exp \ osed}{1,000 \ f \ eet \ row \ X \ wi \ dt \ h}$$

There can also be a calculation of the mg/ft² in the bands themselves, which is done on page 123.

mg ai / ft² =
$$\frac{(12 \text{ oz} / 1000 \text{ ft row}) \times 28,349 \text{ mg} / \text{ oz } \times 9.2\% \text{exp osed}}{1,000 \text{ feet row} \times \text{widt h}}$$

This yields 5.2 mg/ft² (vs 17 in the EFED table).

G.2.2 Aquatic Exposure Corrections

Updated values for environmental modeling are summarized in the section "Modeling Input for Chlorpyrifos-Differences in Interpretation" found in Appendix B. Refined model parameter estimates are used with GENEEC to obtain more representative EECs using this simplistic Tier I screening process. However, GENEEC or PRZM/EXAMS are not appropriate models to use with granulated material (Appendix C).

The typical use rate on corn is a single chlorpyrifos application at 1.2 oz a.i. per 1000 ft row [Lorsban 15G granular insecticide (clay granule)]. Assuming the row spacing is 30 inches, then the corresponding application rate is 1.31 lb chlorpyrifos per acre. However, since T-band applications incorporate granules into the soil, only a fraction of the chlorpyrifos application will be available for runoff. Detailed information is known about the spatial distribution of granules in soil following a T-band application (Hummel et al., 1992; Erbach and Tollefson, 1983; Fischer and Best, 1995; Idema et al., 1993; Tollner and Cryer, 1997). This information is summarized in tabular form in Appendix D, where the mean and standard deviation for the amount of active present in the runoff susceptible surface layer of soil is $7.3 \pm 7.3\%$. Following U.S. EPA recommendations for obtaining a single value from a distribution of numbers as listed below (R.D. Jones, April 1998),

% of applied at soil surface = mean + $(t_{90} * \sigma) / \sqrt{n}$,

the overall percent of applied at the soil surface available for runoff is approximately 9.2% (mean = 7.3, σ = 7.3 t_{90} = 1.315, n = 26). Since GENEEC does not accurately account for T-band spatial distributions of granules in soil (nor for chlorpyrifos release rates from granules (Appendix C)), it is assumed that a broadcast application rate is made (i.e., 0.0 cm incorporation)

but the magnitude of the rate is scaled by 9.2%. Thus, the T-band application rate of 1.31 lb/A is more realistically approximated as a surface broadcast application at a rate of 0.12 lb chlorpyrifos per acre (1.31 lb/A * 0.092) since it is known that only 9.2% of applied is within the upper soil surface layer susceptible to runoff. GENEEC simulation results are tabulated in the table below. The most conservative assessment for a granule using GENEEC is to have all of the active material available for runoff on the day of application since GENEEC assumes a major storm occurs immediately near this date. However, a granule can slowly release chlorpyrifos mass over time and thus the actual mass available for runoff following an application will be much less than what either PRZM or GENEEC can simulate. Higher tiered exposure assessments are performed to account for this behavior (Havens et al.,1994, 1998).

Crop	Use rate	Peak EEC ¹ (ppb)	4-day average EEC (ppb)	21-day average EEC ² (ppb)	56-day average EEC (ppb)
Corn (Iowa and	1 application at 1.2 oz per 1000	0.321	0.234	0.0784	0.0308
Mississippi)	ft row				

¹Acute exposure value for RQ

G.2.3 Corrected Tables for Typical Corn Use: (pp 128-130)

Corrected Use Pattern from Appendix A.1

Granular Risk Quotients for the Typical Corn Use Rate (Iowa) (At-Plant, 7-inch Band or T-Band; 1 Application at 1.2 oz./1,000 Feet of Row; 1-inch Soil Incorporation) (Terrestrial EEC's Based on Formula*; Aquatic EEC's Based on Formula** and GENEEC Model)					
Species	Toxicity	Exposure	Toxicity Dose (mg a.i./LD50	Risk Quotient New/Old	
Mammalian Acute LD ₅₀ (15 grams body wt.) (35 g body wt.) (1000 g body wt.)	193 mg/kg	1.3 mg/ ft ² *	2.9 mg 6.8 mg 193 mg	0.45 /1.1 0.19 / 0.50 0.007 / 0.018	
Avian Acute Oral LD ₅₀ (27.7 g body wt.)	111 mg/kg	1.3 mg/ft ² *	2.77 mg	0.47 /6.1	
Freshwater Fish Acute LC ₅₀	3.4 ppb	0.3 ppb		0.09 /1.9	
Fish Reproduction NOEC	0.57 ppb	0.1 ppb		0.18 /2.5 - 4.6	
Aquatic Invertebrate Acute LC ₅₀	0.55 ppb	0.3 ppb		0.55 / 34	
Freshwater Invert. Reproduction NOEC	0.061 ppb	0.1 ppb		1.6 /35 - 65	
Estuarine Fish Acute LC ₅₀	1.3 ppb	0.3 ppb		0.23 / 3.5	

²Chronic exposure value for RO

Estuarine Fish Reproduction NOEC	0.28 ppb	0.1 ppb	0.36 /5.0 - 9.3
Estuarine Invertebrate Acute LC ₅₀	0.043 ppb	0.3 ppb	7.0 / 97
Estuarine Invert. Reproduction NOEC	0.003 ppb	0.1 ppb	33 />300 ->570
Estuarine Algae EC ₅₀	140 ppb	3.4 ppb	0.024

G.3 Alfalfa Lorsban 4E Insecticide Example

G.3.1 Terrestrial Exposure Corrections

Alfalfa Typical (.75 lb/acre) scenario, based on field monitoring data analysis in Appendix D.1.2

	· · · · · · · · · · · · · · · · · · ·	<u> </u>	
surrogate species	new exposure values (ppm)	notes	reference
Herbivores	3.75	seed maximum	Booth, 1989
	175	grass maximum	Booth, 1989
Insectivores	7	insects ¹	Gallagher et al., 1994.
Granivores	3.75	seed maximum	Booth, 1989
Subacute Dietary	3.75	seed maximum	Booth, 1989
	175	grass maximum	Booth, 1989
Reproduction NOEL	3.75	seed maximum	Booth, 1989
	175	grass maximum	Booth, 1989

¹Distinction not made between large and small insects

G.3.2 Aquatic Exposure Corrections

Updated values for environmental modeling are summarized in the section "Modeling Input for Chlorpyrifos-Differences in Interpretation" found in Appendix B. Refined model parameter estimates are used with GENEEC to obtain more representative EECs using this simplistic Tier I screening process. However, GENEEC extrapolations on dense crops such as turf or alfalfa are outside of the valid range the model is based upon.

GENEEC is not an appropriate tool to use for alfalfa since applications are made directly to plant leaf surfaces (i.e., foliar dissipation and wash-off of the pesticide can occur before even reaching the ground surface to become available for runoff, which GENEEC does not account for). In addition, water infiltration and runoff rates are different between grass and bare soil, and most researchers resort to model calibration procedures of reducing the SCS runoff curve number to match experimental observations (Lin and Graney, 1992; Wauchope et al., 1990). Even tables recommending which runoff curve number to use for various hydrologic soil-cover complexes

have pasture or range curve numbers substantially reduced from those of row crops indicating dense vegetation such as turf or alfalfa yield low water volume runoff and sediment yields (Knisel, 1993).

Since GENEEC is based on bare soil/row crop agricultural uses of PRZM/EXAMS modeling, extrapolations to alfalfa (or turf) are not scientifically justifiable without adjustments to model hydrology (i.e., curve number) and erosion parameters. These following extrapolations are only provided as an example of the exposure refinement possible using systematically generated single value model input parameters (Appendix B).

GENEEC results for the alfalfa typical use rate (a single application at 0.75 lb/A) are provided in the table below.

Crop	Use rate	Peak EEC ¹ (ppb)	4-day average EEC (ppb)	21-day average EEC ² (ppb)	56-day average EEC (ppb)
Alfalfa	1 application, 0.75 lb/acre	2.88	2.22	0.74	0.29

¹Acute exposure value for RQ

²Chronic exposure value for RQ

G.3.3 Corrected Use Pattern from Appendix A.1

Typical Alfalfa Use (p 134)

Risk Quotients for Typical Use on Alfalfa (Post-emergent, Foliar Spray; 1 Application at 0.75 lb a.i./A) (Terrestrial EECs Based on Nomograph; Aquatic EECs Based on GENEEC Model)

Surrogate Species	Exposure	Toxicity (LC ₅₀)	Risk Quotient New/Old
Mammalian Herbivores LD_{50} (15 g body wt.) (35 g body wt.) (1000 g body wt.)	3.8 - 175 ppm	213 ppm 307 ppm 1351 ppm	0.018 - 0.82 /0.10 - 1.6 0.012 - 0.57 /0.071 - 1.1 0.003 - 0.13 /0.016 - 0.26
$\begin{array}{c} \text{Mammalian Insectivores LD}_{50} \text{ (15 g body wt.)} \\ \text{(35 g body wt.)} \\ \text{(1000 g body wt.)} \end{array}$	7 ррт	213 ppm 307 ppm 1351 ppm	0.033 /0.10 - 0.93 0.023 /0.071 - 0.65 0.005 /0.016 - 0.15
$\begin{array}{c} \text{Mammalian Granivores LD}_{50} \text{(15 g body wt.)} \\ $	3.8 ppm	965 ppm 1351 ppm 6757 ppm	0.004 /0.023 0.003 /0.016 <0.001 /0.003
Mammalian Subacute Dietary LC ₅₀	3.8 - 175 ppm	1330 ppm	0.003 - 0.13 /0.008 - 0.13
Mammalian Reproduction NOEL	3.8 - 175 ppm	10 ppm	0.38 - 17 /1.1 - 17
Avian Subacute Dietary LC ₅₀	3.8 - 175 ppm	253 ppm	0.015 - 0.69 /0.077 - 1.2
Avian Reproduction NOEL	3.8 - 175 ppm	25 ppm	0.15 - 7 /0.42 - 6.7
Freshwater Fish Acute LC ₅₀	2.9 ppb	3.4 ppb	0.85 /2.0
Fish Reproduction NOEC	0.7 ppb	0.57 ppb	1.3 /3.0 - 5.5
Aquatic Invertebrate Acute LC ₅₀	2.9 ppb	0.55 ppb	5.3 /36
Freshwater Invert. Reproduction NOEC	0.7 ppb	0.061 ppb	11/52 - 78
Estuarine Fish Acute LC ₅₀	2.9 ppb	1.3 ppb	2.2 /3.7
Estuarine Fish Reproduction NOEC	0.7 ppb	0.28 ppb	2.5 /6.1 - 11
Estuarine Invertebrate Acute LC ₅₀	2.9 ppb	0.043 ppb	67 / 100
Estuarine Invert. Reproduction NOEC	0.7 ppb	0.003 ppb	233 /> 370 > 680

G.4 Turf Example, Dursban 4E Specialty Insecticide

G.4.1 Terrestrial Exposure Corrections

Turf Typical (1.0 lb/A) scenario, based on field monitoring data analysis in Appendix D.1.2

<u> </u>	<u> </u>	 	
surrogate species	new exposure values (ppm)	notes	reference
Herbivores	5	seed maximum	Booth, 1989
	233	grass maximum	Booth, 1989
Insectivores	27	insects ¹	Gallagher et al., 1994.
Granivores	5	seed maximum	Booth, 1989
Subacute Dietary	5	seed maximum	Booth, 1989
	233	grass maximum	Booth, 1989
Reproduction NOEL	5	seed maximum	Booth, 1989
	233	grass maximum	Booth, 1989

¹Distinction not made between large and small insects

G.4.2 Aquatic Exposure Corrections

Limitations to turf modeling have previously been summarized (Appendix G.2) and often entail calibration to existing field observations. A turf runoff study for chlorpyrifos (Racke et al., 1994) has been performed using both bluegrass and bermudagrass on artificially irrigated small plots approximately 0.08 acres in size on moderate to severe slopes (5.8 - 12.6%). Observations of runoff water (no chemical) leaving the plot were between 9.2 - 15.3% of applied precipitation for simulated storms with return frequencies of 1-in-10 to 1-in-50 years. Even with such intense precipitation events, only 0.02 - 0.07% of applied chlorpyrifos were observed to leave the turf field. A value of 0.0632% of applied is used as the percentage of applied predicted to runoff using the t₉₀ methodology of USEPA (R.D. Jones, April 1998).

A typical turf application rate is 1.0 lb/A [1121 g/ha] (Appendix A.2). Assuming a 10 ha turf field draining into a 1 ha pond (2-meters deep), the resulting water concentration can be calculated as

Runoff mass lost from turf field = 1121 g/ha * 10 ha * (0.0632/100) = 7.08 g Volume of water = 1 ha * 10,000 m²/ha * 2 m * 10^6 cm³/m³ = 2.0 x 10^{10} cm³ Peak water concentration = 7.08 g/2.0 x 10^{10} cm³ = 0.354 ppb

 $^{^{1}}$ $\mu = 0.045\%$, $\sigma = 0.0238\%$, n = 4, $t_{90} = 1.533$

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The 4, 21, and 56 day average water concentrations can be calculated using the function listed below (assuming an aerobic aquatic half-life for chlorpyrifos of 7.08 days (Appendix B) with first order dissipation).

$$C_o \int_0^t e^{-kt} dt$$
 Concentration average = $\frac{0}{t-0}$, where

 C_o = instantaneous pond concentration (i.e., 0.354 ppb)

 $k = first order rate constant [ln(0.5)/t_{1/2} = 0.69315/7.08 = 0.0979 day^{-1}]$

t = time average of interest (i.e., 4-day, 21-day, etc).

Crop	Use rate (typical)	Peak EEC ¹ (ppb)	4-day average EEC (ppb)	21-day average EEC ² (ppb)	56-day average EEC (ppb)	90-day average EEC (ppb)
Turf	1 application at 1.0 lb/acre	0.354	0.293	0.150	0.064	0.0402

¹Acute exposure value for RQ

This is an appropriate technique to estimate exposure values for turf scenarios in lieu of more complex and realistic turf modeling, since the use of GENEEC is outside the limits and assumptions on which it is based.

²Chronic exposure value for RQ

G.4.3 Corrected Use Pattern from Appendix A.1

Typical Turf Use (pp 193-194)

Risk Quotients for Typical Golf Course Turf Use (Ground Spray Treatment; 1 lb a.i./A; 1 Application) (Terrestrial EEC's Based on FATE Model; Aquatic EEC's Based on GENEEC Model)

(Terrestrial EEC's Based on FATE Model; Aquatic EEC's Based on GENEEC Model)							
Secies	Exposure	Toxicity (LC50)	Risk Quotient New/Old				
Mammalian Herbivores LD ₅₀ (15 g body wt.) (35 g body wt.) (1000 g body wt.)	5 - 233 ppm	213 ppm 307 ppm 1351 ppm	0.023 - 1.1 /5.6 - 9.9 0.016 - 0.76 /3.9 - 6.9 0.004 - 0.18 /0.88 - 1.6				
Mammalian Insectivores LD ₅₀ (15 g body wt.) (35 g body wt.) (1000 g body wt.)	9.3 ppm	213 ppm 307 ppm 1351 ppm	0.04 /0.62 - 5.6 0.03 /0.43 - 3.9 0.007 /0.097 - 0.88				
$\begin{array}{c} \text{Mammalian Granivores LD}_{50} \text{(15 grams body wt.)} \\ $	5 - 233 ppm	965 ppm 1351 ppm 6757 ppm	0.005 - 0.24/0.14 - 1.2 0.004 - 0.17/0.097 - 0.88 < 0.001 - 0.034/0.019 - 0.18				
Mammalian Subacute Dietary LC ₅₀	5 - 233 ppm	1330 ppm	0.004 - 0.18 /0.43 <i>-</i> 0.76				
Mammalian Reproduction NOEL	5 - 233 ppm	10 ppm	0.50 -23 /57 - 100				
Avian Subacute Dietary LC ₅₀	5 - 233 ppm	253 ppm	0.020 - 0.92 /4.2 - 7.4				
Avian Reproduction NOEL	5 - 233 ppm	25 ppm	0.20 - 9.3 /23 - 58				
Freshwater Fish Acute LC ₅₀	0.4 ppb	3.4 ppb	0.12 /16				
Fish Reproduction NOEC	0.2 ppb	0.57 ppb	0.35 /26 - 45				
Aquatic Invertebrate Acute LC ₅₀	0.4 ppb	0.55 ppb	0.73 /290				
Freshwater Invert. Reproduction NOEC	0.2 ppb	0.061 ppb	3.3 /370 - 640				
Estuarine Fish Acute LC ₅₀	0.4 ppb	1.3 ppb	0.31 /30				
Estuarine Fish Reproduction NOEC	0.2 ppb	0.28 ppb	0.71 /52 - 91				
Estuarine Invertebrate Acute LC ₅₀	0.4 ppb	0.043 ppb	9.3 /830				
Estuarine Invert. Reproduction NOEC	0.2 ppb	0.003 ppb	67 /> 3200 > 5500				
Estuarine Algae EC ₅₀	29 ppb	140 ppb	0.21				